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CONTENTS.

VOL. VIII.

Page

Experimental Error in Calorimetric Work. By Spencer Umfreville Pickering, M.A., Professor of Chemistry at Bedford College 1

On Delicate Calorimetric Thermometers. By Spencer Umfreville Pickering, M.A., Professor of Chemistry at Bedford College 8

The Relations of Pressure, Temperature, and Volume in Saturated Vapours. By Prof. W. C. Unwin, M. Inst. C.E. 22

A Map of the World on Flamsteed's Projection. By Walter Baily, M.A. (Plate I.) 32

Note on a "Relation between the Critical Temperatures of Bodies and their Thermal Expansions as Liquids." By T. E. Thorpe, Ph.D., F.R.S., and A. W. Rücker, M.A., F.R.S. .. 34

On the Cause of the Solar-Diurnal Variations of Terrestrial Magnetism. By Professor Balfour Stewart, LL.D., F.R.S... 38

On a Modification of Wheatstone's Rheostat. By Shelford Bidwell, M.A. 50

On a Theorem relating to Curved Diffraction-gratings. By Walter Baily, M.A. 53

Some Thermodynamical Relations.—Part IV. By William Ramsay, Ph.D., and Sydney Young, D.Sc. 56

Some Thermodynamical Relations.—Part V. By William Ramsay, Ph.D., and Sydney Young, D.Sc. 61

On a new Hyperbolograph. By H. Cunynghame 67

On an Electric-light Fire-damp Indicator. By Walter Emmott and William Ackroyd 69

Note on a Mode of maintaining Tuning-forks by Electricity. By Prof. S. P. Thompson, D.Sc., B.A. 72

Page

Further Notes on the Formulæ of the Electromagnet and the Equations of the Dynamo. By Professor Silvanus P. Thompson, D.Sc., B.A. 76

The Expansion of Mercury between 0° C. and −39° C. By Professors W. E. Ayrton, F.R.S., and John Perry, F.R.S. .. 86

On the Expansion produced by Amalgamation. By Professors W. E. Ayrton, F.R.S., and John Perry, F.R.S. 88

On certain Sources of Error in Connection with Experiments on Torsional Vibrations. By Herbert Tomlinson, B.A. 90

On the Distinction between Spectral Lines of Solar and Terrestrial Origin. By Prof. M. A. Cornu. (Plate II.) 95

The peculiar Sunrise-Shadows of Adam's Peak in Ceylon. By the Hon. Ralph Abercromby, F.R.Met. Soc. 101

On the Critical Mean Curvature of Liquid Surfaces of Revolution. By A. W. Rücker, M.A., F.R.S. 108

Influence of Change of Condition from the Liquid to the Solid State on Vapour-pressure. By William Ramsay, Ph.D., and Sydney Young, D.Sc. 119

On the Nature of Liquids, as shown by a Study of the Thermal Properties of Stable and Dissociable Bodies. By William Ramsay, Ph.D., and Sydney Young, D.Sc. 127

Note on a Method of Determining Coefficients of Mutual Induction. By G. Carey Foster, F.R.S. 137

An Account of Cauchy's Theory of Reflection and Refraction of Light. By James Walker, M.A., Demonstrator at the Clarendon Laboratory, Oxford 146

The Permanent and Temporary Effects on some of the Physical Properties of Iron, produced by raising the Temperature to 100° C. By Herbert Tomlinson, B.A. 171

Measuring-Instruments used in Mechanical Testing. By Prof. W. C. Unwin, F.R.S. 179

On an Arc-Lamp suitable to be used with the Duboscq Lantern. By Professor Silvanus P. Thompson, D.Sc. (Plate III.) .. 184

Note on the Tenacity of Spun Glass. By E. Gibson and R. A. Gregory 191

Page

On Evaporation and Dissociation.—Part VI. On the Continuous Transition from the Liquid to the Gaseous State of Matter at all Temperatures. By William Ramsay, Ph.D., and Sydney Young, D.Sc. (Plates IV., V., VI., & VII.) .. 194

On the Determination of Coefficients of Mutual Induction by means of the Ballistic Galvanometer and Earth-Inductor. By R. H. M. Bosanquet 220

On Delicate Thermometers. By Spencer Umfreville Pickering, M.A., Professor of Chemistry at Bedford College 229

On the Effect of Pressure on Thermometer-bulbs, and on some Sources of Error in Thermometers. By Spencer Umfreville Pickering, M.A., Professor of Chemistry at Bedford College .. 234

Index 241

[At end of Volume.]

Proceedings at the Meetings, and Report of the President and Council for the Session 1886–87.

PLATES.

I. Illustrative of Mr. Baily's Paper on a Map of the World on Flamsteed's Projection.

II. Illustrative of Prof. Cornu's Paper on the Distinction between Spectral Lines of Solar and Terrestrial Origin.

III. Illustrative of Prof. Thompson's Paper on an Arc-Lamp suitable to be used with the Duboscq Lantern.

IV., V., VI., & VII. Illustrative of Drs. Ramsay and Young's Paper on Evaporation and Dissociation.

PROCEEDINGS

OF

THE PHYSICAL SOCIETY

OF LONDON.

May 1886.

I. *Experimental Error in Calorimetric Work.* By Spencer Umfreville Pickering, *M.A., Professor of Chemistry at Bedford College*[*].

The determination of the heat of dissolution of a solid in water is an operation which will always occupy a most important position in the majority of calorimetric determinations; and it is therefore desirable to ascertain what the experimental error involved in this process is, and in what direction we must look for a reduction of this error. The large number of these determinations which I have had occasion to make during the last two years will give the means requisite for an investigation of this error.

The *modus operandi* in the experiments was as follows:—The given salt was weighed out into test-tubes on feet, which were placed in an open metal beaker carefully guarded from radiation and draughts by screens; in this was suspended a delicate thermometer, a companion instrument to that used in the calorimeter itself, the exact difference in the readings between the two instruments being known throughout the extent of their scales.

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[*] Read February 13, 1886.

It was found that one hour * was a sufficient interval to allow for the salt to assume the temperature of the surrounding atmosphere, provided this latter remained constant during this time. In order to diminish the error in measuring the rate of cooling (or heating) during the dissolution of the salt, the temperature of the air was always maintained as nearly as possible at the temperature of the calorimetric water, the difference in the majority of cases not exceeding ·1° C., or at the most ·2° C. The correction to be applied, owing to the temperature of the salt not being exactly the same as that of the calorimetric water, was thus rendered very small, and in most cases quite negligible.

The alteration in the temperature of the salt during its removal to the calorimeter can scarcely be appreciable, since this operation does not take more than ten or fifteen seconds.

The calorimeter employed was an open calorimeter similar to that devised by Berthelot (*Mécanique Chimique*, vol. i. p. 140); a pounder such as Berthelot uses to crush salts which cake (*ibid.* vol. i. p. 183) being employed in all cases, not only as a pounder, but also as a stirrer, and the platinum vessel in which the operations were performed being always used without its cover; indeed, free circulation of air round the calorimeter is most important in all delicate determinations. It was found that an annular cardboard disk, covering in a most imperfect manner the space between the calorimeter and the surrounding water-jacket, enclosed the air to an extent sufficient to make it act as so much calorimetric water, and introduced a very appreciable error into the results.

In dissolving an anhydrous salt, when caking generally occurs, the calorimeter proper cannot be placed on the cork tripod as in other cases, but must be supported on a cork disk covered with cardboard; and, inasmuch as this disk was found to absorb an appreciable amount of heat from the calorimeter, the quantity thus absorbed had to be determined by performing a series of experiments in which a reaction of known calorimetric value was effected in the calorimeter when supported on the tripod and on the disk alternately. The use of this disk unfortunately introduces a small experimental error, since from continual pounding the form of the bottom of the platinum vessel is altered, and consequently this vessel may not be in such intimate contact with the disk at one time as at another, and the amount of heat absorbed by the latter will therefore not always be the same. The error thus introduced, however, cannot be very large, since the disk was never found to be equivalent to more than one hundredth of the contents of the calorimeter.

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* A hygroscopic substance may be left in a tube well closed with an india-rubber stopper for two or three hours with safety; but a longer exposure should be avoided, as moisture is gradually absorbed from the air permeating the stopper.

It was thought possible that an error might also arise in the following manner. Before the introduction of any salt into the calorimeter, all the parts of the apparatus are at the same temperature; but as soon as a reaction takes place, involving, say, the evolution of heat, the radiation from the calorimeter will raise the temperature of the vessel which is interposed between it and the water-jacket (owing to its great bulk the water-jacket itself remains practically unaltered in temperature). During the rest of the time allowed for the experiment this vessel will therefore be at a higher temperature than it was initially; and consequently the rate of cooling during the last intervals will be less than during the first one, the correction to be applied for cooling will be under-estimated, the intermediate vessel having in reality acted as so much calorimetric water. In order to ascertain whether the error from this source attained appreciable dimensions, four experiments with potassium sulphate were performed; in two of these the intermediate vessel was present as usual, while in the other two it was dispensed with. The results obtained were as follows:—

A. With the intermediate vessel:—

$$\left.\begin{array}{l} 1.\ \ldots\ldots\ -7215 \text{ calories} \\ 2.\ \ldots\ldots\ -7181 \quad ,, \end{array}\right\}\text{Mean} \quad -7198 \text{ cal.}$$

B. Without the intermediate vessel:—

$$\left.\begin{array}{l} 1.\ \ldots\ldots\ -7157 \text{ calories} \\ 2.\ \ldots\ldots\ -7185 \quad ,, \end{array}\right\}\text{Mean} \quad -7171 \text{ cal.}$$

Showing that the use of the intermediate vessel had no appreciable effect on the results obtained *. Where, however, large heat-disturbances take place in the calorimeter, it is safer to dispense with it entirely; and indeed the employment of it is in no case attended by any advantage.

The time required to complete the dissolution of the salt varied, of course, in different cases, but rarely exceeded 5 minutes. The loss (or gain) of heat by radiation &c. during this interval was determined separately in each experiment. It was found that with the apparatus employed, and with a difference between the temperature of the calorimetric liquid and that of the surrounding air not exceeding 2°·5 C., the rate of cooling was practically constant throughout the 20–30 minutes (and even for a considerably longer period) during which the experiment lasted; whereas for accurate measurements it was never safe to trust to the results of one experiment to determine the rate of cooling in another experiment, even though the two were performed within 10 minutes of each other, and apparently under exactly similar conditions To determine the rate of cooling, therefore, all the operations (pounding, stirring, &c.), performed during the first 5 minutes to effect the dissolution of the salt, were imitated as nearly as possible during a second, third, and sometimes even fourth and fifth similar intervals, the temperature being read at the end of each interval. The actual rate of cooling (or heating) rarely exceeded 0°·04 C. for 5 minutes, and was generally much less.

In these experiments the proportion of salt to water taken was 1 : 400 molecules†, the actual volume of the latter being about 600 cub. centim. The chief salts operated on were the sulphates of sodium, potassium, lithium, copper, magnesium, potassium-magnesium, and potassium-copper, both hydrated and anhydrous.

The thermometers were all read by estimation by means of a lens to the twentieth part of the marked divisions, *i. e.* to 0·05 millim.‡; and one such estimation-figure, being equivalent to ·002° C., makes a difference of about 16 cal. in the molecular heat of dissolution. I should not put the estimation-figure at less than one tenth of the marked divisions were it not that these experiments afford ample proof that some reliance can be placed on smaller amounts than this.

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* If otherwise, the results of A would be smaller than those of B.

† With double salts 1 : 800; but, for the sake of comparison, these are here reduced so as to be comparable with the other experiments.

‡ The divisions in some of the instruments measured rather more than

The heat-disturbance in the calorimeter varied between *nil* and 2°·3 C., the average being rather less than 1° C.

Out of some 600 determinations of this nature, I may discard the first hundred as consisting chiefly of preliminary and imperfectly conducted experiments; the next century of determinations was also found to give an experimental error decidedly higher than the rest; these also I have therefore omitted, and will confine myself to the remaining 400 experiments. Out of these, however, it will only be the ones which were performed in duplicate which will be available for the present purposes.

Now the average difference between two such duplicate experiments, performed on the same day and with one thermometer only in the calorimeter, was found to be 26·6 calories (deduced from 76 separate experiments), giving a probable error in each experiment of ±13·3 cal.; this corresponds to an error in the thermometric column of considerably less than ±·05 millim.; and as the results involve not only four or five readings of the thermometer, but also the correct reproduction of every action performed in dissolving the salt during the intervals allowed for the determination of the rate of cooling, the correct determination of the salt temperature, and many other points where serious experimental error may occur, I consider that I am fully justified in concluding that the thermometers can be read to ·05 millim., and that even a certain amount of reliance can be placed on such estimation figures.

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1 millim., namely 1·2 millim.; but, provided sufficient attention be paid to a certain proportion between the breadth of the mercurial column and the distance between the divisions, there is no appreciable difference between estimating the fractional portions of these two quantities. Besides practice, and uniformity in the lines themselves, nothing conduces so much to accuracy in estimation as a just proportion between the breadth of the mercurial column and the distance between the divisions. I find the best proportion to be 1 : 10; 1 : 15 is too great, and 1 : 5 too small. Different ratios, however, might suit different observers.

Where the duplicate experiments were not performed on the same day, the error was found to be greater than in the previous case; on an average, deduced from such experiments, it amounted to ±19·6 cal. This number is, however, somewhat bigger than it should be for strict comparison with the previous one; for the experiments which yielded it belonged chiefly to the earlier ones amongst the 400 under consideration, and an increase of accuracy appeared to be made with increased practice throughout the whole series.

In what follows I deal with those duplicate experiments which were performed consecutively only. We thus have so far:—

I. Difference of two experiments where one thermometer was employed, 26·6 cal.

Now in a large number of cases two thermometers were used in the calorimeter at the same time; from these was deduced,

II. Difference of two experiments where two thermometers were employed, taking the results obtained with the same instrument in the two experiments, 41·9 cal. (from 72 experiments).

Subtracting I. from II., we get

III. 15·3 cal. as the increase of difference in two experiments due to the increased difficulty of manipulation when two thermometers are used instead of one.

IV. Difference in two experiments when two thermometers are used, comparing the results obtained with the one instrument in the one experiment with those of the other instrument in the other experiment, 53·02 cal. (from 76 experiments).

V. Difference in the results obtained from the two different thermometers in the *same* experiment, 33·95 cal. (from 142 experiments).

Now, subtracting II. from IV., we get

VI. That portion of the difference in the results given by two thermometers in any single experiment which is due to the instruments not being absolutely concordant, 11·12 cal.

(This amount will represent the sum of the errors in the calibration and standardization of the instruments. As it is dependent on two readings of each instrument, the amount attributable to each reading will be 3·7 cal., corresponding to ·014 millim., or 0·00056° C.)

Subtracting this amount from V. gives

VII. Difference due to the error inherent in reading the two thermometers, 22·83 cal., and therefore a difference due to error in reading each thermometer of 11·42 cal.

Subtracting these two quantities from I. and II. respectively, and halving the results, we obtain :—

A. In a single experiment where one thermometer is used:—

(1) Error of reading	±5·71 cal.*
(2) Error due to manipulation ...	±7·59 „
Total	±13·3 „

B. In a single experiment where two thermometers are used:—

(1) Error of reading	±11·42 cal.
(2) Error due to manipulation ..	± 9·53 „
Total	±20·95 „

These duplicate experiments being performed at exactly the same temperature, no difference will appear between them due to errors of calibration or standardization ; but in regarding the absolute value of the numbers deduced from them, this source of error must also be taken into account. The amount of this error has already been shown to be 11·12 cal. when the results of two instruments are compared (VI.) ; the total error, therefore, in experiments where one thermometer is used will have to be increased by half this amount, thus becoming ±18·86 cal. This number, then, represents the probable divergence from the truth of any one experiment ; and, from the manner in which the various thermometers were standardized (by comparison with each other), this error will probably be as great when two experiments performed at different temperatures are compared, whether they were performed with the same or with different instruments.

Perhaps, for the purpose of determining this probable error, the calculations ought to be based on the difference between duplicate experiments performed *not* on the same day, in which case the error would be somewhat larger. I have not done so, however, chiefly owing to uncertainty in the number given for this quantity (see above). Many causes also which tend to increase the difference when the experiments are not performed consecutively might not apply in general. Amongst these I may mention the very hygroscopic nature of many of the salts taken, where a difference in the state of moisture of the atmosphere would affect the extent to which traces of water were absorbed during their exposure while being transferred to the weighing-tubes: these substances, again, were often kept in sealed tubes containing sufficient for two or three determinations only, and the contents of the various tubes may not have been dried to precisely the same degree.

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* Corresponding to ·021 millim. of the mercurial column.

II. *On Delicate Calorimetric Thermometers.* *By* Spencer Umfreville Pickering, *M.A.*, *Professor of Chemistry at Bedford College*[*].

In the foregoing communication it has been shown that the average error of a determination of the heat of dissolution of a salt in $400H_2O$ amounts to ±18·86 cal.; but this is only an *average*, and it must not be overlooked that the error in some cases may exceed this very considerably. It is not uncommon to find a difference of 40 or 50 cal. between two duplicate experiments (although the average error in such cases is only ±13·3 cal.), and a proportionately larger error must therefore be expected occasionally in the comparison of two experiments at different temperatures.

The determinations from which these conclusions were drawn consisted of a series of experiments with various salts at temperatures ranging from 1° to 26° C., where it was imperative that the greatest possible accuracy should be attained, and also that the experiments at the different temperatures should all be strictly comparable with each other. The thermometers employed had a range of 15° C., and a total length of 600 millim.; it was therefore impossible to increase their length sufficiently to make one instrument embrace the whole range of 25° C., and any increase in the delicacy (by increasing the size of the bulb) would have involved a diminution in their range, so that more than two instruments would have been required, while in such experiments it is obviously of the greatest importance that as few instruments as possible should be used.

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[*] Read February 13, 1886.

With a view to overcoming these difficulties the following expedient was adopted, whereby the delicacy of the instrument was increased six- or sevenfold, its range was made to embrace that of all temperatures at which a mercurial thermometer can be used, and its registration was rendered (for these purposes) practically independent of calibration and standardization error.

The principle on which it was worked consisted in removing a portion of the mercury, by the application of heat, into the upper chamber, and thus adjusting any particular point in the instrument so as to register any required temperature. Experiments on the same substance at different temperatures were thus made absolutely comparable, exactly the same portion of the scale being used in each case.

The zero point of the thermometer being thus altered for each experiment, the actual temperature in degrees Centigrade which it registers will not be known with any great degree of accuracy; but this is not necessary in calorimetric work: the heat of chemical combination is affected to such a small extent by temperature, that an error of ·05° or ·1° C. in this will be unimportant; and by a rough comparison of the thermometer with some standard instrument after each adjustment of the mercury, the temperature which it registers can be easily ascertained within ·01° or ·02° C.

This thermometer (No. 62839) possessed a total length of 746 millim., of which 565 millim. constituted the divided portion of the stem, each division being 1 millim., and ten such divisions being termed 1 degree. The bulb measured 72 millim. in length, and was made out of glass cylinder instead of being blown, a detail which is rarely attended to in the construction of delicate thermometers, but one which is most important in giving the bulb greater stability and greater uniformity of action. The weight of mercury in the bulb was 36·23* grams, and the total range of the instrument only 3°·4 C., giving 166 millim. to each degree C.; one estimation figure (·05 millim.) would therefore represent ·0003° C.

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* In the other instruments, with a range of 15° C., the weight of mercury varied between 13·6 and 15·6 grams; the bore of the tube of No. 62839 would be considerably more than twice as fine as in these. Fuller details respecting these instruments will be found in the Phil. Mag. March 1886.

In using this thermometer it is first suspended in the calorimeter containing water at a temperature a certain known degree above that at which the experiments are to be made; a very small flame is then applied to a point just below the upper chamber (which in such instruments must be of considerable size), by which means the column of mercury is broken off at the part thus heated, and the separated portion remains in the upper chamber, the tube being much too fine to permit of it being shaken down again. After cooling it is put into a bath at the required temperature, and compared with some standard instrument. In this way the registration of the thermometer can be adjusted to any required temperature within ·05° C. without the least difficulty; but greater accuracy could be obtained if necessary.

This thermometer was employed in a large number of experiments, and the general results, as will be shown below, proved to be satisfactory. But it possessed one serious imperfection, or, more properly speaking, its delicacy brought into light an imperfection which must be inherent, although it has hitherto been unnoticed in all mercurial thermometers.

As is well known, the bulb of a thermometer does not expand regularly when heated; "en effet," to quote Berthelot's words, "la marche de l'instrument est intermittent, c'est-à-dire que le niveau n'est souvent atteint qu'après une série de petites oscillations" *. To obtain a state of equilibrium the

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* *Méc. Chim.* i. p. 178. It is curious to note that even while Berthelot is warning his readers against this source of error he appears to have fallen into it himself. On p. 163 he gives the results of a comparison of two thermometers placed in a bath of water, the temperature of which was rising, and read simultaneously at intervals of ten minutes; from this and other closely concordant comparisons he finds 6·702 degrees of the one instrument are equivalent to 14·827 of the other; but, on looking more closely at each reading, it will be found that

(1) a rise of 0°·9 in the one corresponds to a rise of 1°·1 in the other.
(2) " 0·7 " " " 2·2 "
(3) " 0·6 " " " 1·5 "
(4) " 1·1 " " " 0·9 "
(5) " 1·2 " " " 1·1 "

Vastly discordant numbers.

thermometer must be tapped on the top with the finger, or some such means adopted to overcome the inertia of the bulb before each reading. The larger the bulb and the finer the bore of the tube, the more apparent does this inertia become : with instruments such as the less delicate ones here mentioned a dozen or less taps are sufficient to overcome it, but with No. 62839 it was found that continuous tapping for two or three minutes was absolutely necessary. The extent to which error from this source may accumulate may be drawn from the fact that this instrument, when the mercury is *rising* to the temperature of the bath in which it is placed, will register 6 millim. lower than when *falling* to the same temperature, however long it be left in the bath, if it be not tapped (the temperature of the bath in this case was such that the mercury stood at about the middle point of the stem). Again, it was found, by means of a series of experiments in which the height of the column was read when the instrument was inclined at different angles, that with thermometer 55082, which possessed a blown bulb containing 15·6 grams of mercury, a difference of 6·6 millim. in the reading was made when the instrument was placed horizontally instead of vertically; making due allowance for the greater size of the bulb and greater fineness of the bore in 62839, this latter instrument would probably exhibit a difference of at least ten times this quantity under similar treatment. This will give some adequate idea of how great an effect the expansion of the bulb under pressure may have on the reading.

Now, besides the inertia of the bulb, which may be overcome by a sufficient amount of tapping, there appears to be another and more serious imperfection, due to what may be termed a permanent alteration in size, as opposed to the other, which may be called temporary, and one which no amount of tapping will overcome. It would seem that the bulb of this, and every thermometer, has two different shapes, one when the column is rising, the other when it is falling. The following simple experiments will serve to show this.

The thermometer being suspended in the calorimeter full of water, the contents of this were heated or cooled slightly, and the rate of cooling (or heating) determined during consecutive intervals.

In the first column the time is entered, in the second the reading of the instrument, and in the third the rate of cooling or heating.

A. Experiments in which a rate of *heating* was determined.

I.

Time.	Reading (arbitrary).	Rate.	
0	−1°		
Hot water added.			
1 min.	19·96		
4 „	20·07	·11	
7 „	20·165	·095	mean = ·10.
10 „	20·245	·08	
13 „	20·38	·135	
16 „	20·47	·09	

II.

Time.	Reading.	Rate.	
0	−5°		
Hot water added.			
2 min.	20·685		
5 „	20·76	·075	
8 „	20·855	·095	mean ·09.
11 „	20·94	·085	
14 „	21·03	·09	

In this case the rate of heating is constant from the very beginning: during the first three minutes it differs from the mean of the other intervals by +·01 in Exp. 1 and by −·015 in Exp. 2, both of these quantities being well within the limits of experimental error.

III.

Time.	Reading.	Rate.	
0	54°		
Cold water added.			
2 min.	20·555		
5 „	20·56	·005	
8 „	20·65	·09	mean ·093.
11 „	20·735	·085	
14 „	20·84	·105	

IV.

Time.	Reading.	Rate.	
0	54°		
Cold water added.			
2 min.	19·45		
5 „	19·465	·015	
8 „	19·555	·09	
11 „	19·645	·09	mean ·103.
14 „	19·775	·13	

In these two experiments, however, this is not so; the rate of heating (as registered) during the first interval is almost *nil*, in each case exactly ·088 less than the mean deduced from the other intervals. Thus, when the column of mercury rises to any temperature it will go on rising regularly afterwards, indicating the rate of heating correctly, but when it *falls* to that temperature a certain time elapses before it will begin to rise afterwards; although the mercury must be expanding during this interval, the column is stationary, and therefore the bulb must be expanding, and assuming a new form.

The following experiments are complementary to the preceding ones and illustrate the same fact.

B. Experiments in which a rate of *cooling* was measured.

I.

Time.	Reading.	Rate.	
0	55°		
Cold water added.			
3 min.	22·16		
6 „	21·76	·41	
9 „	21·41	·34	
12 „	20·99	·42	mean ·39.
15 „	20·59	·40	

II.

Time.	Reading.	Rate.	
0	53°		
Cold water added.			
3 min.	22·21		
6 „	21·84	·37	
9 „	21·48	·37	
12 „	21·155	·325	mean ·342.
15 „	20·815	·34	

The difference between the rate of cooling measured during the first interval and that during the remaining ones being +·02 in the one experiment, and +·028 in the other, *i. e.* practically *nil.*

III.

Time.	Reading.	Rate.	
0	0		
Hot water added.	°		
2 min.	20·65		
5 "	20·45	·20	
8 "	20·09	·36	mean ·34.
11 "	19·79	·30	
14 "	19·42	·37	

IV.

Time.	Reading.	Rate.	
0	−3°		
Hot water added.			
1 min.	25·58		
4 "	25·36	·22	
7 "	24·935	·425	mean ·40.
10 "	24·52	·415	
13 "	24·16	·36	

The difference between the first and remaining intervals being −·14 and −·18 in the two experiments. Thus whichever be the direction of the motion of the mercury it will continue in that direction, giving correct results, but, if the direction be changed, an interval elapses before the motion becomes apparent, and a considerable error will be introduced.

The above are but typical experiments out of a large number performed, and all of which gave the same results; indeed, every determination of the heat of dissolution of a salt afforded a fresh exemplification of the fact.

Of course the alteration in the size of the bulb will invalidate any experiment unless its effect be counteracted. This was always done in every experiment by taking care that, if a rate of cooling was to be measured after the salt had been dissolved, the liquid should be cooling also before its introduction, and *vice versâ*; the motion of the mercury, and therefore the shape of the bulb, being the same at the beginning and end of the experiment, no error would occur. In such an experiment, where for instance a rate of cooling obtained, and the salt dissolved with absorption of heat, no period of inertia in the column would occur ; but if the salt dissolved with evolution of heat, two such periods would occur, and, though this would not affect the accuracy of the results, a certain time would elapse before the apparent rate of cooling became constant, extending often to three intervals of 3 or 5 minutes each (for the whole of these intervals cannot be spent in tapping the thermometer as in the experiments quoted above, but are chiefly occupied in reproducing the actions performed in effecting the dissolution of the salt), thus creating a serious increase in the duration of an experiment. This was obviated by removing the thermometer from the calorimeter, touching the bulb with some warm object, when, on replacing it, the column fell to the temperature of the calorimeter, and proceeded to give the rate of cooling at once ; where a rate of heating was to be determined, the thermometer was cooled (by evaporation from the surface) instead of heated. As a few millim. rise or fall are sufficient for the purpose, the heating or cooling of the contents of the calorimeter in such an operation is quite negligible *.

The change of size in the bulb, as deduced from the experiments already quoted, is, perhaps, somewhat exaggerated, owing to an under-estimation at the time of the amount of tapping which was necessary to overcome the temporary inertia of the bulb. The following, even more simple, experiments are free from such an error, and bring to light other facts concerning this phenomenon.

The method of procedure here consisted in suspending the thermometer in a calorimeter containing a much larger volume of water than the one generally used, taking the instrument out, heating and cooling it alternately, when, on its being replaced, readings of the same temperature were obtained, the column having fallen or risen to that temperature respectively.

As it was found to be impossible to keep the temperature of the bath constant during the requisite time, any observed

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* The water-equivalent of the immersed portion of this thermometer was 2·09 grams, that of the calorimeter and contents about 610 grams. A heating of the former sufficient to produce a rise of 5 mm. would raise the temperature of the latter only 0·0001° C.

reading, say when the column was rising to the temperature, was compared with a theoretical reading consisting of the mean of the previous and subsequent readings, both of which were obtained when the column was falling to the temperature. The differences here quoted will represent the total difference between the readings with rising and falling columns. After the thermometer had been replaced in the bath, it was tapped continuously and read at intervals of one minute till it became quite stationary; between five and seven such readings were made in the series here given, although it will be necessary to quote the final reading only in each case. An interval of about 8 minutes elapsed between these final readings, all the intervals in each separate series being exactly equal.

I.

	Registered.	Theory.	Difference.
	°	°	
Immersed after being heated 10°	14·08		
" " cooled 10	14·08	14·103	−·023
" " heated 10	14·125	14·118	+·097
" " cooled 10	14·155	14·185	−·030
" " heated 30	14·245	14·233	+·012
" " cooled 10	14·310	14·313	−·003
" " heated 10	14·380		
		Mean	·015

II.

	Registered.	Theory.	Difference.
	°	°	
Immersed after being cooled 10°	26·83		
" " heated 10	26·86	26·845	+·015
" " cooled 10	26·86	26·908	−·048
" " heated 10	26·955	26·918	+·037
" " cooled 10	26·975	27·008	−·033
" " heated 10	27·06	27·038	+·022
" " cooled 20	27·10	27·123	−·023
" " heated 20	27·185	27·175	+·010
" " cooled 10	27·25		
		Mean	·027

III.

	Registered.	Theory.	Difference.
	°	°	
Immersed after being heated 10°	45·845		
" " cooled 10	45·755	45·804	−·049
" " heated 10	45·763	45·718	+ 045
" " cooled 10	45·680	45·717	−·063
" " heated 10	45·670	45·643	+·027
" " cooled 10	45·605	45·655	−·045
" " heated 10	45·640	45·595	+·045
" " cooled 10	45·585	45·635	−·050
" " heated 10	45·630		
		Mean	·046

Without exception, therefore, a reading when the thermometer is falling to a given temperature is higher than when it is rising to this same temperature, and the difference between these two readings appears to be independent of the extent of the foregoing fall or rise; a fact which will be shown more clearly in a series of similar experiments with another thermometer to be quoted below. The difference in the two readings, however, is considerably influenced by the position of the mercury in the stem; from these experiments it would appear to be directly proportional to the height of the column, the total difference in each case being $\frac{1}{1000}$ of this height.

Although this difference is very appreciable, it must be remembered that it corresponds to a difference of very small dimensions in the capacity of the bulb. The $0^\circ\cdot015$ measured in the first series is equivalent to $0^\circ\cdot0009$ C., and represents but 0·0000004 c.c., or but little over one millionth part of the total capacity of the bulb (2·64 c.c.), a quantity so small that there is no wonder in its having hitherto escaped observation. The considerable force necessary to push a column of mercury through a long very fine tube is, I should say, quite sufficient to account for this expansion of the bulb; it is well illustrated by the fact that a quick fall of but a small amount causes the mercury to separate at the neck of the bulb.

The question now arises whether this instrument, possessing such serious imperfections, is really workable, or whether we have not pushed thermometric delicacy beyond the limits compatible with accuracy.

The various determinations of the heat of dissolution of salts which were made with this thermometer give the means of answering this question.

As shown in the previous communication, ±13·3 cal. is the average error of each experiment when compared with a duplicate one performed under the same conditions; of this 7·59 cal. are error due to manipulation and 5·71 cal. to error of reading. The manipulation-error will be independent of the thermometer employed, but the reading-error will be smaller in direct proportion to the delicacy of the instrument. As an estimation-figure with No. 62839 represents about $\frac{1}{6\cdot4}$ of what it does in the case of the instruments to which these numbers refer, the reading-error with it ought to be only $\frac{5\cdot71}{6\cdot4}$, or about ·9 cal., giving a total error for each experiment of ±(·9 + 7·59 =)8·49.

Now the average difference of two duplicate experiments with this thermometer was found to be 14·84 cal. (deduced from 38 experiments), giving an error of only ±7·42 * cal. for each experiment, a quantity even smaller than that which would have been anticipated, proving conclusively that such an instrument can be worked with just as much certainty as the less delicate ones. The fact that the total error here is even less than the manipulation-error alone in the other experiments is due to greater care being taken in manipulation, a larger number of intervals being allowed for the determination of the rate of cooling. It must be remembered, however, that this diminution of the difference between two duplicate experiments by no means represents the total advantages accruing from the use of this thermometer, for, the same portion of the instrument being used for experiments with the same substance at all the different temperatures, these will be on the same footing as duplicate experiments themselves. We shall, therefore, have to make no addition to this error when comparing different experiments in a series, and we thus get rid at once of the additional error of ±5·56 cal., which had to be admitted with the other instruments †.

The extra time required for experiments with such an instrument is considerable; the determination itself occupies two or three times as long as with an ordinary thermometer, and the preliminary adjustment of the mercury ‡ and the

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[*] I am probably very much overstating the error here; this number is deduced from *all* the experiments in which this thermometer was used. Several of these were performed before the peculiarities of the instrument were thoroughly known, and contained known sources of error; eliminating these, the average error of the remaining experiments (24 in number) is only ±3·33 cal., a surprisingly small quantity.

[†] From what has been mentioned in the Phil. Mag. March 1886 as to the error of standardizing this thermometer, the divergence of any measurement from the absolute value will probably not be more than ·00045° C. for each degree C. measured, or ±3–4 cal.

[‡] In one instrument which I possess a small particle of dust has become fixed in the tube just below the upper chamber, the result of which is that the column of mercury, whenever it has passed a few millimetres beyond this point, breaks off there and shoots up into the upper chamber.

comparison with a standard occupies the greater part of an hour. It is possible to do three determinations at different temperatures with it in a day; but this means a very hard day's work, and could only be effected after much practice.

Although the results obtained with this thermometer may appear satisfactory as measured by the average error, they still leave much to be desired. It is impossible to feel absolute confidence in an instrument which possesses such serious imperfections; and, apart from this, I was desirous of investigating the matter further for its own sake, and producing an instrument in which delicacy did not involve the sacrifice even of convenience.

It occurred to me that the substitution of a double bulb for the single bulb of No. 62839 would probably result in a considerable increase in strength under pressure. Such an instrument, therefore, I had constructed. Considerable difficulty was met with in boiling the mercury in a double bulb thoroughly, but this was overcome in a masterful manner, while at the same time the other parts of the instrument were so perfect that I believe it is the finest thermometer of its kind ever constructed, in this country at any rate. The stem was of the required stoutness, and the bore, while being flat, was well rounded at the edges, thus exposing no crevices into which the mercury would find it difficult to enter, as is usually the case with flat bores, and as was so with No. 62839. The length of each bulb of this instrument, No. 63616, was 55 mm., the total weight of mercury in them being 30·5 grams, considerably less therefore than in the other thermometer and less than double that in the bulbs of some of the less delicate thermometers. The scale was rather less open than in 62839, the total range of 60 cm. representing 3°·85 C., or 154·3 mm. to each degree, one estimation-figure representing therefore $\frac{1}{3000}°$.

The results of two series of experiments with this instrument similar to those with 62839, last described, gave the following results :—

If it were possible to introduce such an obstacle at will, the time expended in separating the mercury by heat, and the danger thereby incurred, would be obviated. I am not without hopes of succeeding in effecting this.

I.

	Registered.	Theory.	Difference.
	°	°	
Immersed after being cooled 1°	45·69		
" " heated 1	45·765	45·688	+·077
" " cooled 1	45·685	45·790	−·105
" " heated 1	45·815	45·703	+·112
" " cooled 10	45·720	45·733	−·113
" " heated 10	45·850	45·768	+·082
" " cooled 10	45·815	45·899	−·084
" " heated 10	45·947		
		Mean	·096

II.

	Registered.	Theory.	Difference.
	°	°	
Immersed after being heated 10°	13·985		
" " cooled 10	13·95	14·00	−·05
" " heated 10	14·015	13·93	+·085
" " cooled 10	13·91	14·029	−·119
" " heated 10	14·043	13·933	+·110
" " cooled 10	13·955	14·044	−·089
" " heated 10	14·045		
		Mean	·091

Thus, contrary to expectation, this instrument not only shows a difference in reading when the column is rising or falling to any temperature, but that difference is even greater, and considerably so, than with No. 62839. This is certainly remarkable, and tends to show that a full explanation of this difference has not yet been obtained, for the double bulb would undoubtedly possess a greater rigidity than the single bulb of the other instrument; although the combined length of the two bulbs is 110 millim. as opposed to 72 millim., the diameter of the tubing of which they were made was considerably less, 4·83 millim. instead of 6·86 millim. (internal measurements), and the wall of the tubing also was considerably stouter, 0·76 millim. instead of 0·635 millim., and a small improvement in these last two items would cause a very considerable increase in the rigidity. Another peculiarity in this instrument is that the difference in the readings is independent of the height of the column of mercury; or at any rate very nearly so.

Series I. of the above experiments affords good proof that the difference in readings is independent of the distance through which the column has fallen or risen; the mean difference of the first three numbers in the last column being

·098, and that of the last three ·093; numbers practically identical, although the fall or rise was 1 degree in the former, and 10 degrees in the latter.

Although this difference, due to what I have termed the permanent alteration in the size of the bulb, is greater with 63616 than with 62839, it is otherwise with the temporary alteration. An experiment similar to the above, but the tapping of the instrument being omitted, gave a difference of 0°·23 in the mercury standing at 45·8, whereas with 62839 it amounted to 0°·6 (at 27°); these numbers representing the sum of the permanent and temporary alterations, the latter only will be represented by (·23 − ·096 =) 0°·13, and (·6 − ·027 =) 0°·57 in the two instruments respectively. This tends to confirm an opinion expressed by Mr. Casella, that a considerable portion of this temporary alteration is due, not to the bulb, but to the mercury not entirely filling the bore of tube of its own accord, owing to the extreme flatness of this latter at the edges. The tube of which 63616 was made presented no such imperfections. However, neither the permanent nor temporary difference can be in any degree attributed to the action of the tube in this latter instrument, but is wholly due to the bulb itself; for the thermometer was first made up with a small bulb*, containing only 3 grams of mercury, in which state it showed no difference whatever in the readings obtained under different conditions, with or without tapping. The comparative smallness of this temporary alteration in the case of 63616 renders this instrument far more convenient and satisfactory than the other. Instead of requiring two or three minutes continuous tapping in order to obtain a correct reading, less than one minute is sufficient, and this must very materially increase accuracy in calorimetric determinations. I have not as yet used this thermometer in a sufficient number of experiments to ascertain the experimental error with it; but the uniformity of its action and the increased concordance of the rate of cooling registered in successive intervals, leads me to feel confident that the error with it will be considerably less than with 62839.

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* Where the bulb is to contain as much as 20 or 30 grams of mercury, it is well to have the instrument made up temporarily with a small bulb, for the purpose of calibration, as with fine tubes some rough handling is often necessary to pass a short thread of mercury along them.

It would appear that 30 grams of mercury is not an uncommon amount in the instruments used by Berthelot (*Méc. Chim.* i. 165), although they are far less delicate than those described in the present communication. He even refers to thermometers containing 250 grams! (p. 156).

From what has already been said as to the smallness of the reading-error in this instrument, it may be stated that we have pushed thermometric delicacy quite as far as is desirable with regard to calorimetric work, and that to produce a further degree of accuracy in this branch of study, the methods employed, and not the thermometers, must be improved.

In conclusion, I wish to take this opportunity of expressing my warmest thanks to Mr. Casella and to his assistants for the scientific interest which they have shown in this investigation, and the ungrudging manner in which they have spared no pains to help me in attaining my object.

III. *The Relations of Pressure, Temperature, and Volume in Saturated Vapours.* *By* W. C. UNWIN, *M. Inst. C.E.**

IN the interesting and laborious paper of Messrs. Ramsay and Young, there are given four relations of a simple kind between the pressures, temperatures, and volumes of saturated vapours and the heat of vaporization of a number of substances. These relations are not given as exact relations, but as suggestive of laws approximately satisfied by very different substances over a very wide range of conditions.

Now long ago Hirn pointed out that, as for saturated vapours there exists only a single value of p and t corresponding to one specific volume v, there must be a direct relation between t and v, and between p and v, independent of p or t. But hitherto no exact relation has been found, and we remain still in the condition of being obliged in every thermodynamical calculation to fall back at every step on data either interpolated from tables of experimental values, or determined by the aid of purely empirical formulæ. Nor is this all: the formulæ are themselves cumbrous and are not interrelated.

Regnault's formula, giving p in terms of t for instance, cannot be inverted to get t in terms of p, though in practical calculations the pressure is almost always the given datum. Further, if differentiated to obtain $\frac{dp}{dt}$ an expression is obtained far too cumbrous for ordinary use. Rankine's formula is nearly as accurate, and is both simpler and gives an inverse function; but the expression for $\frac{dp}{dt}$ is cumbrous. The expression for latent heat is necessarily independent, but then the density or specific volume ought to be expressed in terms of the formulæ for latent heat and pressure and temperature. But there being no simple expression for $\frac{dp}{dt}$ it is more common to resort to the quite independent empirical formula of Zeuner.

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* Read February 27, 1886.

For purely scientific purposes no absolute difficulty or inaccuracy is caused, and no advance can be hoped for till rational expressions are found. When such expressions are found, also, it may probably prove, as Hirn surmises, that they will not have the simplicity which some people expect in all natural laws. The practical difficulty, again, can be surmounted by means of the tabulated values of p, t, $\frac{dp}{dt}$, calculated with great care and labour by Prof. Zeuner and Prof. Cotterill. Nevertheless the author thinks that some clearness would be introduced into the teaching of thermodynamics, and possibly some facility gained in practical calculations, if only amongst empirical expressions to which recourse must be had, one could be found accurate enough and yet so simple that all the related functions could be derived from it. The paper of Messrs. Ramsay and Young suggested an attempt in that direction.

It might be expected that the approximate relations stated by Profs. Ramsay and Young could be deduced from some of the empirical relations already established. This, however, is not strictly the case.

It is known for instance that the expression

$$p = \mathrm{AT}^{5\cdot 5},$$

where A is a constant and T is reckoned from an arbitrary zero, approximately satisfies the law connecting the pressure and temperature of saturated vapours.

Differentiating,

$$\frac{dp}{dT} = 5{\cdot}5\,\mathrm{A}\,\mathrm{T}^{4\cdot5};$$

so that

$$\mathrm{T}\,\frac{dp}{dT} = 5{\cdot}5\,\mathrm{A}\,\mathrm{T}^{5\cdot5} = 5{\cdot}5p.$$

Consequently

$$\frac{\mathrm{T}}{p}\,\frac{dp}{dT} = 5{\cdot}5:$$

a relation which should be approximately satisfied for different vapours.

Thus, for instance, reckoning from the zeros given below we get from the values of $\frac{dp}{dt}$ in Messrs. Ramsay and Young's tables the following values of $\frac{\mathrm{T}}{p}\,\frac{dp}{dt}$:—

Substance ...	Bisulph. of Carbon.	Ethyl Alcohol.	Water.	Mercury.
Zero (Above −273°C)	144°.	208°.	210°.	322°.
Pressure in mm.				
100	5·913	5·323	5·183	5·243
500	5·749	5·616	5·794	5·598
1000	5·666	5·802	5·808	5·707
5000	5·201	5·540	5·645	......
10,000	......	5·429	5·503	......
20,000	......	5·291	5·302	......

At first sight it looks as if this were similar to the relation $t\,\frac{dp}{dt}$ = constant at any one pressure, given in Messrs. Ramsay and Young's paper. But, obviously, it is a quite different relation from the difference in the reckoning of temperature. It is, besides, a purely empirical relation, and the constancy of the values obtained may serve as a useful warning against accepting such correspondence of formula and data as indicating that the formula expresses a real law.

The principal relation discussed by Messrs. Ramsay and Young is that

$$t\,\frac{dp}{dt}$$

is constant for different vapours at the same pressure. In their table (Proc. Phys. Soc. vol. vii. p. 301*) values of this quantity, very carefully and laboriously calculated, are given for various vapours at pressures ranging from 10 to 20,000 mm. of mercury. It will easily be seen that the numbers in each horizontal line in their table approximate to constancy, varying in extreme cases by possibly 30 per cent.

If now these numbers are divided by the pressures so as to form values of

$$\frac{t}{p}\frac{dp}{dt},$$

the constancy of the horizontal lines of figures will remain unaffected, while the vertical columns will approach to constancy almost as nearly as the horizontal columns. The following table gives these values, with some of those for mercury corrected and with those for vapour of carbonic anhydride added:—

Values of $\frac{t}{p}\frac{dp}{dt}$ for different vapours.

Pressure in millims.	Carbon bisulphide, CS_2.	Ethyl bromide, C_2H_5Br.	Ether, $C_4H_{10}O$.	Chloroform, $CHCl_3$.	Mercury, Hg.	Sulphur, S.	Water, H_2O.	Ethyl alcohol, C_2H_5OH.	Carbonic anhydride, CO_2.
100	12·80	13·64	13·04	......	......	......	16·07	16·42	......
500	10·83	11·31	11·22	11·66	13·20	12·12	13·81	14·39	......
1000	10·10	10·37	10·51	10·85	11·89	11·20	12·95	13·83	......
3000	8·68	8·96	9·24	9·27	11·23	9·67	11·58	11·99	......
5000	8·22	8·26	8·66	8·46	9·73	......	10·89	11·29	......
10,000	......	......	......	......	......	......	10·03	10·39	7·62
15,000	......	......	......	......	......	......	9·50	9·89	7·63
20,000	......	......	......	......	......	......	9·13	9·54	7·57
50,000	......	......	......	......	......	......	......	......	6·77

But now it may be pointed out that $\frac{t}{p}\frac{dp}{dt}$ is not a mere arbitrary expression for

$$\frac{t}{p}\frac{dp}{dt}=\frac{r}{\mathrm{A}pu}$$

(Hirn, tom. i. p. 319). That is, it is the ratio between the total heat of evaporation and the heat expended in external work. What we have found, therefore, is that this ratio approaches constancy for widely different substances and under considerable differences of pressure. This approximation to constancy appears to me to lie at the basis of all the relations Messrs. Young and Ramsay have found.

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* Phil. Mag. vol. xx. p. 526 (December 1885).

The constancy of this ratio of internal and external work, for different vapours at one pressure, has been investigated by Messrs. Young and Ramsay from other data, but it does not seem to have occurred to them that it would be obtained in the simple way given above.

The author noticed that another relation, namely,

$$\frac{t^2}{p}\,\frac{dp}{dt},$$

gave values for each vapour, far more constant at different pressures than

$$\frac{t}{p}\,\frac{dp}{dt}.$$

The following table gives some of these values :—

Values of $\frac{t^2}{p}\,\frac{dp}{dt}$ for different vapours.

Pressure in millims.	Carbon bisulphide, CS_2.	Ether, $C_4H_{10}O$.	Mercury, Hg.	Sulphur, S.	Water, H_2O.	Ethyl alcohol, C_2H_5OH.	Carbonic anhydride, CO_2.
100	3426	3394	7053	......	5218	5049	......
500	3324	3329	7231	8437	4995	4909	......
1000	3313	3321	7247	8275	4932	4956	......
5000	3220	3233	......	7936	4745	4610	......
10,000	......	......	......	.....	4670	4528	1889
20,000	......	......	......	......	4570	4455	1991
50,000	......	......	......	......	......	......	2018

This suggested that probably an empirical relation of this kind could be found expressing the relation of pressure and temperature very simply and with considerable accuracy.

Let, for instance, for steam the values of $\frac{t^{2\cdot25}}{p}\frac{dp}{dt}$ be formed. We get:—

t.	p.	$\frac{t^{2\cdot25}}{p}\frac{dp}{dt}$.
273	4·60	21660
298	23·55	21970
323	91·98	22020
348	288·5	21940
373	760·0	21870
398	1743·9	21830
423	3581·2	21790
448	6717·4	21770
473	11689·0	21950

Where the greatest and least values differ from the mean by only 0·7 per cent. But the expression, the values of which have been found, is integrable. Putting $n+1$ for the index of t, we get for a general approximate relation between the pressure and temperature of vapours,

$$\log_e p = a - \frac{\beta}{t^n}. \quad \dots\dots \tag{1}$$

From this are easily derived the following equations, in which for convenience the logarithms are common logarithms.

$$\log p = a - \frac{b}{t^n} \quad \dots\dots \tag{2}$$

$$t = \left(\frac{b}{a-\log p}\right)^{\frac{1}{n}}. \quad \dots\dots \tag{2 a}$$

$$\frac{1}{p}\frac{dp}{dt} = 2\cdot3025\,\frac{nb}{t^{n+1}}. \quad \dots\dots \tag{3}$$

$$= 2\cdot3025n\,\frac{(a-\log p)^{\frac{n+1}{n}}}{b^{\frac{1}{n}}}. \quad \dots \tag{3 a}$$

$$\frac{t}{p}\frac{dp}{dt} = 2\cdot3025\,\frac{nb}{t^n} \quad \dots\dots \tag{4}$$

$$= 2\cdot3025n(a-\log p). \quad \dots\dots \tag{4 a}$$

For the latent heat, besides the ordinary formula,

$$\mathrm{L} = m - \frac{n}{(a-\log p)^{\frac{1}{n}}}. \quad \dots\dots \tag{5}$$

And consequently if v is the volume in cubic metres of the vapour and s that of the liquid,

$$v-s=\frac{\mathrm{JL}}{t\frac{dp}{dt}}$$

$$=\frac{13{\cdot}497\mathrm{L}}{pn(a-\log p)}. \quad . \quad . \quad . \quad . \quad . \quad (6)$$

In all these equations the quantity required is expressed simply in terms of the pressure or the temperature, a result not obtainable with the formulæ previously used.

Formulæ for Steam.

To test the value of these equations, the author has calculated the constants for steam most suitable for the complete range of Regnault's experiments, from −30° C. to 230° C., and from 0·4 millim. pressure to 20,000 millim. pressure. The proposal of a new empirical formula, and one not so accurate as Rankine's or Regnault's, for the relation of p and t in the case of steam, will probably appear the reverse of commendable. Still the fact that it gives a series of expressions, all directly derived from it, simple enough for ordinary use in engine calculations and accurate enough for practical purposes, is a strong reason in its favour. Its applicability can only be determined by testing its accuracy in a sufficient number of cases. In all the following calculations the calculated values are compared with the most accurate values thus far computed, over a range of pressure and temperature greater than would occur in practical cases.

The primary equation, derived from Regnault's data, for millimetres of mercury, Centigrade degrees reckoned from −273° C., and common logarithms is

$$\log p=7{\cdot}5030-\frac{7579}{t^{1{\cdot}25}}, \quad . \quad . \quad . \quad . \quad . \quad (7)$$

which gives

$$t=\left(\frac{7579}{7{\cdot}5030-\log p}\right)^{\frac{4}{5}}. \quad . \quad . \quad . \quad . \quad . \quad (7a)$$

The following table gives the values of *p* calculated from *t* with Regnault's experimental values and values calculated by Rankine's formula for comparison :—

Temperature, Centigrade.	Temperature, absolute.	Pressure in millims. Regnault.	Pressure in millims. by formula.	Error in millims.	Pressure in millims. by Rankine.	Error in millims.
−30°	243°	0·386	·401	+ ·015	·35	−·036
−20	253	0·91	·982	+ ·072	·89	−·02
−10	263	2·08	2·229	+ ·149	2·07	−·01
0	273	4·60	4·709	+ ·109	4·47	−·13
5	278	6·53	6·69	+ ·16		
10	283	9·17	9·40	+ ·23	9·05	−·12
15	288	12·70	13·01	+ ·31		
20	293	17·39	17·83	+ ·44	17·33	−·06
25	298	23·55	24·07	+ ·52		
30	303	31·55	32·18	+ ·63	31·57	+·02
35	308	41·83	42·61	+ ·78		
40	313	54·91	55·72	+ ·81	55·05	+·14
45	318	71·39	72·24	+ ·85		
50	323	91·98	92·85	+ ·87	92·26	+·28
55	328	117·48	118·30	+ ·82		
60	333	148·79	149·48	+ ·69	149·15	+·36
65	338	186·94	187·50	+ ·56		
70	343	233·08	233·61	+ ·53	233·48	+·40
75	348	288·50	288·60	+ ·10		
80	353	354·62	353·59	−1·03	355·04	+·42
85	358	433·00	433·21	+ ·21		
90	363	525·39	523·48	−1·91	525·70	+·31
95	368	633·69	633·72	+ ·03		
100	373	760·00	757·35	−2·65	760·0	0
105	378	906·41	904·27	−2·14		
110	383	1075·4	1071·5	−3·9	1074·8	−·6
115	388	1269·4	1263·3	−6·1		
120	393	1491·3	1485·6	−5·7	1490·1	−1·2
125	398	1743·9	1735·4	−8·48		
130	403	2030·3	2020·2	−10·1	2028·0	−2·3
135	408	2353·7	2347·5	− 6·2		
140	413	2717·6	2710·2	− 7·4	2713·8	−3·8
145	418	3125·6	3114·6	−11·0		
150	423	3581·2	3564·5	−16·7	3575·5	−5·7
155	428	4088·6	4064·4	−24·2		
160	433	4651·6	4633·4	−18·2	4643·6	−8·0
165	438	5274·5	5262·6	−12·9		
170	443	5961·7	5941·6	−20·1	5951·2	−10·5
175	448	6717·4	6694·2	−23·2		
200	473	11689·0	11665·4	−23·6	11675·0	−14·0
230	503	20926·0	20951·7	+25·7	20945·0	+19·0

The following short table gives some values of *t* calculated from *p* :—

p.	t.	
	Calculated by (7a).	Observed.
4·60	272·7	273
91·98	322·8	323
760·00	373·2	373
3581·2	423·2	423
11689·0	473·1	473

The following are the derivative expressions. A few values are calculated from each and compared with the values very laboriously calculated by Zeuner from Regnault's formula.

$$\frac{1}{p}\frac{dp}{dt}=\frac{21815}{t^{2\cdot25}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

$$=\frac{(7\cdot5030-\log p)^{\frac{9}{5}}}{441\cdot3}. \quad . \quad . \quad . \quad (8\,a)$$

t.	$\frac{1}{p}\frac{dp}{dt}$.	
	By formula (8).	From Zeuner.
273	·07201	·07150
323	·04932	·04979
373	·03567	·03577
423	·02688	·02685
473	·02090	·02083

$$\frac{t}{p}\frac{dp}{dt}=\frac{21815}{t^{1\cdot25}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

$$=2\cdot8782(7\cdot5030-\log p). \quad (9\,a)$$

t.	p.	$\frac{t}{p}\frac{dp}{dt}$.		From Zeuner.
		By equation (9).	By equation (9 a).	
273	4·60	19·659	19·69	19·52
323	91·98	15·929	15·94	16·08
373	760·00	13·304	13·30	13·34
423	3581·2	11·368	11·37	11·36
473	11689·0	9·890	9·89	9·85

The latent heat of vaporization has hitherto been expressed only in terms of the temperature by the empirical formula

$$L=796{\cdot}23-0{\cdot}695t, \quad . \quad . \quad . \quad . \quad . \quad (10)$$

where t is the absolute temperature, and the smaller terms containing higher powers of t are omitted. From the relation between p and t we get

$$L=799-\frac{894}{(a-\log p)^{\frac{4}{5}}}. \quad . \quad . \quad . \quad . \quad (10\,a)$$

t.	p.	L.		From Zeuner.
		By equation (10).	By equation (10 a).	
273	4·60	606·5	607·0	606·5
323	91·98	571·8	571·7	571·7
373	760·00	537·0	536·3	536·5
423	3581·2	502·3	501·0	500·8
473	11689·0	466·5	465·9	464·3

The new formula (10 a) is more accurate than the one (10) commonly used.

Let v be the volume in cubic metres of a kilogram of steam, and s the volume of the same quantity of water, usually taken at 0·001,

$$v-s=10{\cdot}821\,\frac{L}{p(a-\log p)}, \quad . \quad . \quad . \quad . \quad (11)$$

where p is still expressed in millimetres.

p.	$v-s$.	
	By equation (11).	From Zeuner.
4·60	208·7	210·6
91·98	12·14	12·05
760·00	1·652	1·650
3581·2	·3833	·3839
11689·0	·1255	·1257

Other Vapours.

The following equations may be useful. That for ether agrees extremely well. The mercury equation less well; but the errors are considerably less than those of Rankine's equation in his paper of 1850. The data are all from Regnault.

Alcohol:—

$$\log p = 7{\cdot}448 - \frac{8784}{t^{1{\cdot}29}}.$$

Ether:—

$$\log p = 6{\cdot}9968 - \frac{3047}{t^{1{\cdot}153}}$$

Mercury:—

$$\log p = 9{\cdot}8651 - \frac{597{\cdot}5}{t^{0{\cdot}69}}.$$

Carbonic acid:—

$$\log p = 8{\cdot}4625 - \frac{302{\cdot}8.}{t^{0{\cdot}77}}$$

IV. *A Map of the World on* Flamsteed's *Projection.*

By WALTER BAILY, *M.A.*[*]

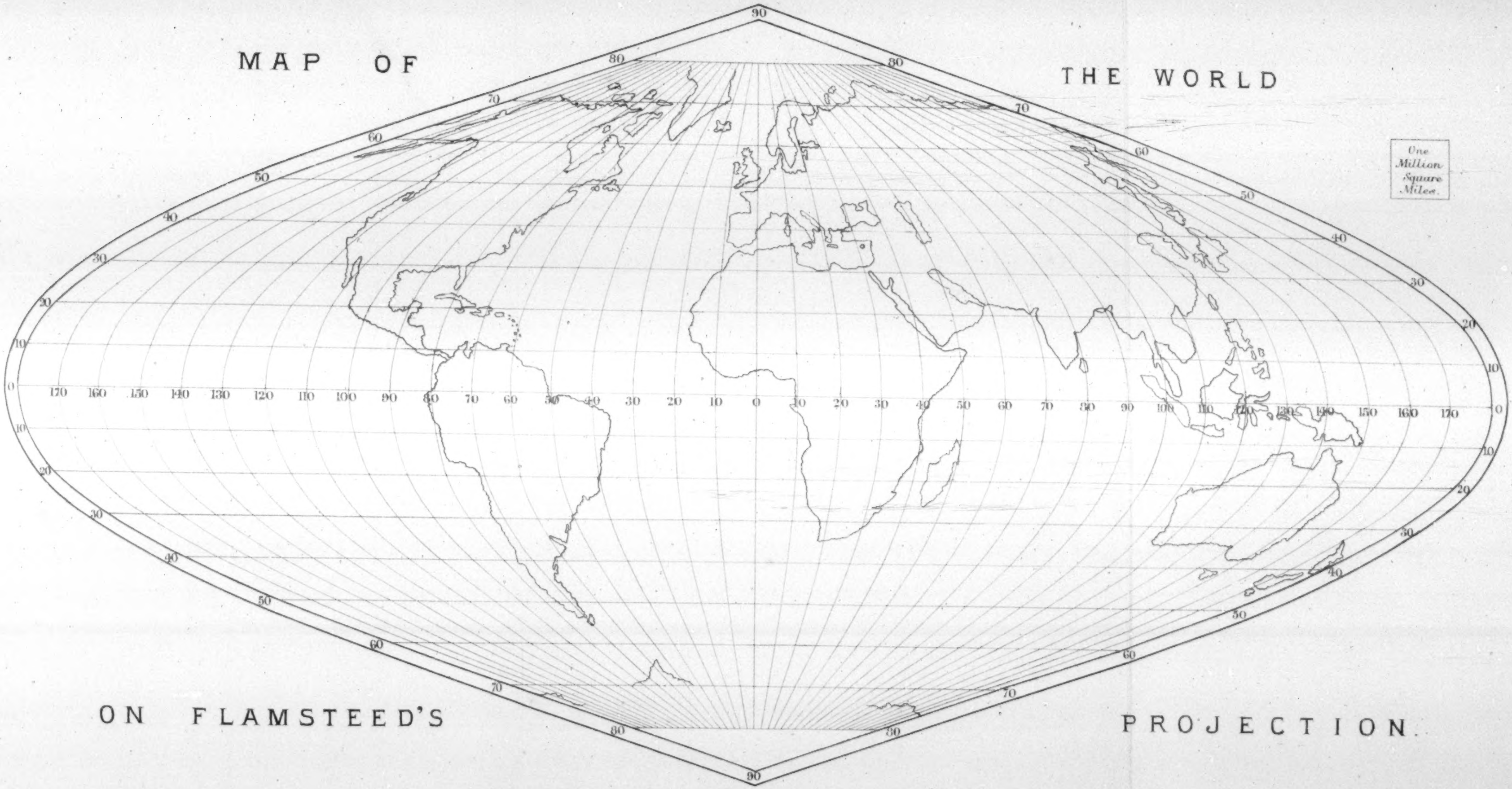
[Plate I.]

IN Flamsteed's *Atlas Cœlestis* the projection used is one invented by him and described in the Preface to that work as follows:—

"Conceive the globe or sphere to be compassed about with an infinite number of infinitely fine threads all exactly parallel to the equator. Let all the circles usually drawn upon the globe, as the equator, the ecliptic, the meridians, &c., be supposed drawn and divided, and let the constellations also be formed upon them, and the stars laid down in their proper places. Let also the meridian passing through the middle of any constellation be conceived drawn on the globe, and covered with a fine thread with as many of the adjacent circles as you may think convenient. Conceive the threads on which the constellation is painted to be cut off from the surface of the globe; and that which passes through the middle being extended straight on the middle of some paper or perfectly plane superficies, let the rest be placed on it at right angles to the middle meridian, but reverted."

[*] Read February 27, 1886.

MAP OF THE WORLD ON FLAMSTEED'S PROJECTION.



Mintern Bros lith.

Flamsteed used his projection only for maps of portions of the celestial sphere, and he did not apply it to the polar regions, as the distortion which would otherwise have been produced would have been inconvenient to an astronomer.

The Preface points out the advantages of the method as follows:—"So will you have the picture of the Constellation projected upon it, in which the parallels of declination will be straight lines and their distances exactly equal, the same as they are on the globe, as will also the distances and differences of the right ascensions of any two stars that are equally distant from the pole." The advantage in Geography of a map in which the parallels of latitude are equidistant straight lines parallel to the equator is obvious, as the position with regard to latitude is seen at a glance. There is, moreover, a property of this projection which is evident at once from the way in which the projection is constructed, viz. that the area of every part is preserved unaltered. The imaginary threads have simply slipped over one another, like the cards in a pack, without altering their distances, so that only a distortion of form has occurred. This property is not referred to by Flamsteed, either because he did not notice it, or because it was of no importance in Astronomy. I venture to submit, however, that in Physical Geography it is a property of considerable importance, and that it would be advisable in many physical maps to use this projection. For instance, in maps showing rainfall, depth of the sea, height of the land, ocean currents, prevailing winds, distribution of plants and animals, &c., it is essential to take account of the area occupied, and maps in which this is correctly shown could not fail to be of use. In Plate I. is shown a map of the World on Flamsteed's projection, the small square at the side representing 1,000,000 square miles on the same scale.

The formulæ for constructing the map are readily obtained. Take the equator as the axis of x, and the central meridian (say the meridian of Greenwich) for the axis of y. Let x, y be the coordinates of a point m° of longitude from the central meridian, and n° of latitude from the equator. Then if α is the length of a degree of latitude in the scale adopted,

$$y/\alpha=n, \quad x/\alpha=m\cos n^\circ.$$

Hence the equation to a meridian m degrees from the central meridian is

$$\frac{x}{a} = m \cos\left(\frac{y}{a} . 1^\circ\right).$$

V. *Note on a "Relation between the Critical Temperatures of Bodies and their Thermal Expansions as Liquids." By* T. E. THORPE, *Ph.D., F.R.S., and* A. W. RÜCKER, *M.A., F.R.S.*[*]

A PAPER bearing the above title was published by us in the Journal of the Chemical Society of London for April 1884, and has recently been discussed by MM. A. Bartoli and E. Stracciati[†]. As these gentlemen have done us the honour to make use of a formula deduced by us from the simple expression given by Mendelejeff for the expansion of liquids, we should like to state exactly the position which we ourselves think ought to be assigned to it, and the use which may legitimately be made of it.

Prof. Mendelejeff has shown[‡] that the expansion of liquids under constant pressure between 0° C. and their boiling-points may be expressed by means of the very simple formula

$$V_t = \frac{1}{1-kt};$$

where V_t is the volume at t° (that at 0° C. being unity), and k is a quantity which differs for different substances, but which may for any one substance be considered invariable between 0° C. and the neighbourhood of the boiling-point.

The great merit of Mendelejeff's law is that it is proved by him to express the law of expansion to within the limits of the differences between the results of different observers experimenting on the same liquid. Thus, if the results of any one observer alone are considered, they may no doubt be most accurately expressed by a formula of the type

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[*] Read April 10, 1886.

[†] *Ann. Chim. Phys.* Mars 1886, p. 384.

[‡] Journ. Chem. Soc. April 1884.

$$V_t = 1 + a't + b't^2 + c't^3.$$

Another equally reliable observer will, however, obtain for the same liquid a formula

$$V_t = 1 + a''t + b''t^2 + c''t^3,$$

where a', b', c' differ appreciably from a'', b'', c''. These slight differences depend on the unavoidable errors of experiment, which may perhaps in the future be diminished, but which at present affect the work of the best observers using the best known methods. Hence formulæ such as those given above can only be considered as approximations to the true law of the expansion of the liquid to which they refer. That law will be most nearly given by combining the results of several physicists whose methods and observations are equally good, rather than of relying upon those of any one.

Now Mendelejeff has shown that the volumes calculated at different temperatures by means of the formula

$$V_t = \frac{1}{1-kt}$$

differ less from the results of good observers than they do from one another. It might in any given case be possible to obtain another more complex formula which would express the *mean result* more accurately, but it would remain very doubtful whether the greater mathematical accuracy obtained represented the physical facts more closely. Mendelejeff (as we think rightly) considers that the simplicity of the formula which he has suggested gives it a special claim upon our attention; and he proves that it expresses, at all events as a first but very close approximation, all *that we certainly know* about the expansion of liquids.

It is therefore no argument against Mendelejeff's formula to remark, as MM. Bartoli and Stracciati have done, that

$$V_t = \frac{1}{1-kt} = 1 + kt + k^2t^2 + k^3t^3 + \&c.;$$

and that in the formulæ given by Pierre, Kopp, Hirn, Thorpe,

&c., the constants *a*, *b*, and *c* do not differ by a constant ratio, as the expression would require. This criticism would only hold good if all these observers had obtained the same, or closely identical, values of *a*, *b*, and *c*; whereas, as a matter of fact, the values of *b* and *c* given by different observers may differ very widely. The very merit of Mendelejeff's remark is that, although the results of no one physicist are expressed by

$$V_t = 1 + kt + k^2t^2 + k^3t^3,$$

yet that this formula in its simpler form,

$$V_t = \frac{1}{1-kt},$$

expresses the results of all as accurately as those results will allow; and that since it is thus sufficiently accurate and extraordinarily simple, it may claim to be the best general formula hitherto proposed for expressing the laws of liquid expansion.

These remarks are subject to the conditions which Mendelejeff made clear, that the formula was only applied to the range of temperature between 0° and the neighbourhood of the boiling-point, and that the constant k increases slightly as the temperature rises. This latter fact indicates that the law, though very accurately expressing the known facts, is only an approximation to the truth.

Mendelejeff's formula, then, appears to us to stand in somewhat the same position as Boyle's or Charles's laws. It is a first approximation, which expresses the facts, under given conditions of temperature and pressure, with great accuracy. The difference between the two cases is that, whereas the deviation of each of the principal gases from Boyle's law has been studied, Mendelejeff has shown that the most careful researches do not enable us to state with certainty what is the magnitude of the error caused by applying his formula to any particular liquid. They show only that k increases very slightly as the temperature rises.

Having thus defined as accurately as we can the position which we think that Mendelejeff's law holds, we need hardly say that we do not claim any higher status for our own formula connecting the law of expansion and the critical temperature.

We were most careful to express in our paper our appreciation of the fact that our expression was based upon Mendelejeff's, and therefore it ranked only as a theoretical deduction from an extremely close approximation to the truth, and is to be employed only under the conditions for which that approximation was valid.

Thus we have shown that the critical temperature of a liquid (T_c) is given very approximately by the formula

$$T_c = \frac{TV - 273}{a(V_t - 1)};$$

where V_t is the volume at $t°$ C., $T = 273 + t$, and a is a constant which we proved is nearly $= 2$.

We should, however, never have thought of applying this formula to determine the critical temperature of water from the expansion up to 200° C. We have not applied it to water at all, on account of the well-known peculiarities of the expansion of that substance; but had we done so, we should have regarded it as holding only between 0° C. and the boiling-point. We have distinctly laid it down that it is under these conditions k is to be determined*. In proving, therefore, that the values of the critical temperature, calculated from the expansions at temperatures above the boiling-point, vary very widely from those obtained under the conditions adopted by Mendelejeff and ourselves, MM. Bartoli and Stracciati have only shown that the formula does not hold good under circumstances to which its authors never intended it to be applied.

We are, however, gratified to find that these gentlemen, notwithstanding their criticisms, show a reliance upon our formula even greater than that which we feel ourselves. The values of the constant a given in our paper prove that its true value is uncertain, at all events to 1 per cent. or more. MM. Bartoli and Stracciati, however, give in their second paper a number of critical temperatures calculated by the formula to tenths of a degree. If the tenth of a degree is to be determined with accuracy, the constant a must be known to 0·025 per cent.

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* Journ. Chem. Soc. *loc. cit.* p. 139.

VI. *On the Cause of the Solar-Diurnal Variations of Terrestrial Magnetism.* *By* Professor Balfour Stewart, *LL.D., F.R.S.*[*]

In attempting to account for the Solar-diurnal inequalities of Terrestrial Magnetism, scientific speculators have ranged over the whole field of likely explanations. Some of them think that they have now finally driven the truth into a corner, and are in hopes of ultimately securing the object of their pursuit.

I shall begin by enumerating the chief hypotheses which have been proposed.

(1) There is, first, that of the direct magnetic action of the Sun upon the Earth. There are, however, many serious objections to this hypothesis. One of these is the great difficulty attending the supposition that the Sun is capable of acting as a powerful magnet, since terrestrial analogies would lead us to infer that matter at the high temperature of the Sun is quite incapable of possessing magnetic properties. Again, we have strong evidence that changes in the range of the daily variation of magnetic declination lag behind corresponding solar changes in point of time. This kind of behaviour is apparently inconsistent with direct magnetic action, and points rather to some indirect influence probably caused by the radiant energy of the Sun, inasmuch as the changes and turning-points of such indirect influences due to radiation are well known to lag in respect of time behind the corresponding changes and turning-points in their cause. Finally, Dr. Lloyd and Mr. C. Chambers[†] have both shown that direct solar magnetic action will not account for the peculiarities of the diurnal magnetic variation. We may therefore perhaps dimiss this hypothesis.

(2) The next hypothesis which I shall introduce is that of Faraday. Reasoning from his discovery that oxygen is magnetic and becomes weaker in its power when heated, he concludes that when the Sun heats a certain portion of the Earth's atmosphere, this renders that portion less magnetic

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[*] Read April 10, 1886.

[†] Proc. Royal Irish Academy, Feb. 22, 1858, and Phil. Trans. 1863.

than those other portions not subjected to solar influence. This kind of action is thus seen to be equivalent to a displacement by means of solar influence of the magnetic matter of the Earth, and hence implies a corresponding displacement of the lines of magnetic force. Now there is unquestionably truth in this hypothesis, but yet there is very great doubt whether it will account for the diurnal oscillation as we know it. It will form *a cause*, but yet it will not be *the chief cause.* It is obviously one prominent peculiarity of Faraday's hypothesis, that in it the action of the Sun must, to ensure its probability, be associated with the great mass of the Earth's atmosphere, that is to say with the lower strata as well as with the upper; or rather with the lower strata in preference to the upper, bearing in mind the superior mass of the former and their greater nearness to the magnetic Earth. Now we know both from observations of the declination and horizontal force (Proc. Roy. Soc. March 22, 1877, and Phil. Trans. 1880, p. 541) that the action of the Sun in producing diurnal variations of these elements is one and a half times as powerful at epochs of maximum as it is at epochs of minimum sun-spot frequency.

But it is very difficult, if not impossible, to imagine that the great mass of the atmosphere can be heated by the Sun one and a half times as much at epochs of maximum sun-spot frequency as it is at epochs of minimum sun-spot frequency; and yet we must imagine this if we suppose that Faraday's hypothesis accounts for the diurnal variation. Certainly the facts of meteorology are strongly against any such belief. Again, during our summer the heating influence of the Sun is considerably greater in the Northern than in the Southern Hemisphere, while during our winter the reverse will be the case. Totally apart from the diurnal variation we ought therefore, if Faraday's hypothesis be true, to find a very perceptible difference in the mean magnetic condition of the Northern Hemisphere between summer and winter, and a like difference too in the Southern Hemisphere, the one being at the same moment differently affected from the other. But there are no traces of such a phenomenon, the annual and semi-annual variations being quite of a different nature and none of them very large.

(3) Let me now discuss the hypothesis that these variations are caused by earth-currents. These currents were first detected by W. H. Barlow, and were at a later period observed and studied by C. V. Walker. They are now continuously recorded by photography at the Royal Observatory, Greenwich, and at the Central Russian Observatory.

With respect to these currents, I have always maintained that in type they bear all the marks of being secondary currents generated in the moist conducting crust of the Earth, and caused by small but abrupt changes in the magnetism of the Earth. Whether this be the true explanation or not, it is at any rate, I venture to think, consistent with what we know of electrical action. But while I should thus feel disposed to regard these phenomena as effects rather than causes, in their primary sense at least, it is manifest that, when once generated, such currents will influence the needle; and the results of the Greenwich observers induce us to think that such influence is very great and forms perhaps the chief immediate cause of those oscillations of the needle called disturbances, which are quite different from the solar diurnal variation. In one sense therefore such currents may be effects, while in another they are causes, but causes of disturbances rather than of the daily variation.

It may, however, be replied that earth-currents may be complex phenomena, and that while their most important manifestations may be due to induction, thus being primarily effects rather than causes, yet another portion of them may operate as a true cause producing the solar-diurnal variation. Now there are two objections to this hypothesis; and one of these is, that we know of no physical agency that will produce in the Earth's crust currents of this nature, which, in order to account for the solar-diurnal variation, must be one and a half times more powerful at times of maximum than at times of minimum sun-spot frequency. Another objection is that Sir George Airy has not been able to detect any resemblance in form between the regular diurnal progress of the magnet and that of the earth-currents. We think therefore that we may dismiss this hypothesis.

Now, if it be unlikely that these magnetic variations are caused either by the direct magnetic action of the Sun, or by earth-currents, or by the heating effect of the Sun on the chief mass of the Earth's atmosphere, we seem to be driven by the method of exhaustion to look for their cause in the upper atmospheric regions. We shall, however, have to show that there is no improbability in locating their cause in these elevated regions, otherwise our method of exhaustion will have done us no service. In the first place, I need hardly say that if the cause we are in search of be in these upper regions, it must either be in the shape of a set of electrical currents, or in some other shape with which we are quite unacquainted; but the nature of this discussion precludes us from entertaining the latter supposition; and we are therefore driven to regard electrical currents as being the only conceivable cause, if this cause is to be located in the upper atmospheric regions.

I shall now attempt to reply to two imaginary objections that may be raised as to the possibility of such currents. In the first place, it may be said that while undoubtedly rarified air is a conductor of electricity, yet it is not a good conductor; and where can we look for sufficient potential to drive currents through these upper atmospheric regions? To this I would reply that *as a matter of fact* we know that there are visible electric currents in the upper atmospheric regions which occur occasionally at ordinary latitudes, and which are very frequent, if not continuous, in certain regions of the Earth. I allude to the Aurora, which is unquestionably an electric current, and must therefore influence the magnetic needle. Furthermore, both with respect to its times of occurrence and to the disposition of its beams, the Aurora manifests a close connection with the phenomena of terrestrial magnetism, occurring at ordinary latitudes only when there are great magnetic disturbances, and the disposition of its beams having a distinct reference to lines of magnetic force. We are therefore justified in asserting that there is no impossibility in conceiving a set of electrical currents, intimately associated with certain phenomena of terrestrial magnetism, to exist in the upper region of the Earth's atmosphere.

In the next place, the objection may be raised, How is it possible to suppose any cause that will make such currents one and a half times more powerful at times of maximum than at times of minimum sun-spot frequency? Can it be imagined that the radiant energy of our luminary varies in this proportion? Now it has been remarked by Professor Stokes that an increase in the radiative power of the Sun would most probably imply, not only an increase in general radiation, but a special and predominant increase in such actinic rays as are probably absorbed in the upper regions of the Earth's atmosphere. These regions will therefore greedily absorb the new rays, their temperature will rise, and, as is known to be the case for gases, the electrical conductivity of the strata will be increased*. Thus, even if we imagine the general atmospheric current to remain constant, a greater proportion of it would be thrown at such times into those heated regions which had become good conductors; but then it is likewise probable that the current itself would be increased as well as increasingly diverted into a particular channel.

Such an explanation appears to receive support from the curious and suggestive fact that the lunar influence on the Earth's magnetism, as observed at Trevandrum, is greater during the day than during the night, and greater perhaps, too, at times of maximum than at times of minimum sun-spot frequency. If the arguments now advanced be generally assented to, we may presume that, while it is unlikely that the cause of the daily variation exists anywhere else than in the upper regions of the Earth's atmosphere, there is no objection to our imagining that it resides there in the form of a set of electric currents. Such currents will of course affect the needle directly, but they will also affect the magnetic earth, and any affection of the magnetic earth will again influence the needle. The question thus arises, To what extent do these hypothetical currents act directly upon the needle, and to what extent do they act upon it indirectly by influencing the magnetism of the Earth? That this question is not unimportant will be manifest by considering what takes place when a powerful electromagnet influences a needle. In this case probably only a small portion of the influence is due to the direct action of the current, while a large portion is due to the iron of the electromagnet that has been magnetized by the current. In order to study this point it will perhaps be desirable that we limit ourselves to the solar diurnal variations of declination, as these are of a simple definite type in each hemisphere, the type in the one hemisphere being the reverse of that in the other. Let us therefore consider the peculiarities of this variation, particularly in the regions on either side of the magnetic equator.

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* It seems not impossible, too, that the constitution of these strata with respect to aqueous vapour, may be different at times of maximum and at times of minimum sun-spot frequency; hence their absorbing power may be different.

Here we find, speaking generally, that north of the equator the extreme westerly deflection of the marked pole of the needle is reached at 2 P.M., while south of the equator this pole reaches its extreme easterly deflection at the same hour. Now, if we attempt to picture to ourselves any general change in the magnetic system of the Earth that will produce these results, it will be one of a very artificial character. On the other hand, these motions of the needle, which cannot well be explained by any easily conceivable temporary change of the Earth's magnetic system, can very easily be explained by a system of atmospheric currents. In the northern hemisphere we should have a set of positive currents flowing from the equator northwards, while in the southern we should have in like manner a similar set of positive currents flowing southwards. And, therefore, since positive currents flow out from the equator on both sides of it, we should have to contemplate a vertical stream of positive electricity at the equator which there splits itself up into two portions—one for each hemisphere.

The argument as I have now advanced it is of a general nature and is twofold.

(1) In the first place it brings forward objections to the localization of the cause of the diurnal variations anywhere else than in the higher regions of the Earth's atmosphere; then points out that if this cause exist in these regions it must be in the shape of a system of electric currents; and finally endeavours to show that there are no valid objections to such a system of currents.

(2) It endeavours to show that, if we take the diurnal

variation of the declination-needle, which is of a remarkably simple type, we have great difficulty in imagining that it can be brought about by any temporarily induced displacement of the magnetic system of the earth, while we can with the greatest ease account for it by means of a system of currents in the upper regions of the Earth's atmosphere.

At this point Dr. Schuster has endeavoured to apply mathematical analysis to the subject, and he has obtained results which are very satisfactory and encouraging *. He had previously, in the Report of the Magnetic Committee of the British Association for the year 1885, pointed out the existence of a test † which will enable us to decide whether or not the diurnal variation can be caused by a series of electric currents which embrace both the upper atmospheric regions and the Earth, and complete themselves by electric discharges through the lower regions of the Earth's atmosphere into the ground; and he now endeavoured to ascertain whether the supposed vertical currents at the equator, to which allusion has been made, could possibly be of this nature. If this were the case, he argues, and if a unit pole were carried from a position A at the Earth's surface in a path which should return again to A, and in the centre of which there should exist such a vertical current, then through all its course work would be done either by or against this pole, inasmuch as there would be a continued effort of the vertical current to turn the pole round it in one direction. In other words, the pole and the point A being immersed in the system of currents, there would be a potential having multiple values. On the other hand, if the system which produces the daily variation be outside of A, whether above or below it, there will be at A a true potential, and if the unit pole be carried as before, in any path from A and back to A again, as much work will be done against the pole as will be done by it. Let us consider, now, a little path embraced between two parallels of latitude near each other, and two meridians of longitude likewise near each other, and imagine our pole to be carried round this boundary. On the

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* Proc. Lit. & Phil. Society of Manchester, January 12, 1886; Phil. Mag. April 1886, p. 349.

† The reader will find a complete discussion of this subject in Maxwell's 'Electricity and Magnetism.'

supposition that there is no vertical current in the centre of the path, the work done upon the pole will be equal to that done by it. This will at once give us an equation between X and Y; that is to say, between the components of the solar-diurnal periodic force towards the geographical north and west respectively. From this equation, and by means of certain legitimate assumptions regarding the type of Y, which represents very nearly the force influencing the declination (and this we know to be of a simple uniform type), Dr. Schuster is able to obtain certain relations between the solar-diurnal variations of the declination and of the horizontal force which ought to hold, *if there be no vertical currents between the upper regions and the Earth*, or, rather, if such vertical currents are inoperative as an element in producing the solar-diurnal variation. One of these is that the northerly or horizontal-force component of the daily variation ought to have a maximum or a minimum at the time when the westerly or declination component vanishes, that is to say attains its mean position.

Now at Greenwich, X or the horizontal-force component has a maximum at 7 o'clock in the evening and a minimum at noon; while Y or the declination component vanishes a little after 7 o'clock and between 12 and 1 in the afternoon. At Bombay the declination-needle is at its mean value on an average a little after 10 in the morning and about 10 in the evening. The horizontal force has its maximum a little after 11 in the morning and the minimum at a quarter past 9 in the evening.

The observations at Lisbon and Hobarton show an equally good agreement, those at St. Helena and the Cape of Good Hope less so; but in these two latter places the observations taken at different months show a considerable difference of behaviour. On the whole, Dr. Schuster regards the agreement as satisfactory, and as so far tending to disprove the existence of vertical currents through the Earth's surface. Pursuing his analysis, he comes to the conclusion, from certain approximate expressions which he obtains, that the northerly force ought to be a maximum in the morning and a minimum in the afternoon in the equatorial regions; while in latitudes above 45° the minimum ought to take place in the morning.

Now this is almost exactly what happens. At Bombay, for instance, the *maximum* of horizontal force takes place at 11 A.M., while at Greenwich the *minimum* takes place a little after that time.

Having thus obtained results which lead him to infer that the unit pole we are observing is not immersed in the attracting system, Dr. Schuster next proceeds to discuss the question whether this system is above us or beneath us. To do this it is necessary first of all to obtain an approximate value for the potential at the surface of the earth, and from it to derive the general potential. To aid in determining this we must bear in mind that, since the unit pole is now assumed not to be immersed in the attracting system, the potential V will be subject to the condition

$$\frac{d^2V}{dx^2}+\frac{d^2V}{dy^2}+\frac{d^2V}{dz^2}=0$$

or to an equivalent condition adapted to the system of coordinates employed. From this Dr. Schuster deduces two possible expressions for the potential; the one referring to a system above our heads and having powers of (r) the radius in its numerator, the other referring to a system beneath our feet and having powers of the radius in its denominator. Now the expression for the vertical force as derived from the potential will be $-\frac{dV}{dr}$, the sign of which will be manifestly different according as r appears in the numerator or in the denominator of the potential in question. Which, therefore, of these two possible (approximate) forms of V agrees best with observation? In the first place, both expressions found by Dr. Schuster have their turning-points coincident in epoch with those for X, or the northerly component of the disturbing force; and this is a fact confirmed by actual observation. But while the expression for the vertical force derived from a system above us has its maxima and minima coincident with those of horizontal force at latitudes greater than 45°, in the equatorial regions the maximum of horizontal force ought to be coincident with the minimum of vertical force, and *vice versâ*. Precisely the opposite arrangement should hold if the attracting system be beneath our feet.

Now at Greenwich the maximum of northerly force takes place at 7 P.M. and the minimum at noon; while the maximum of vertical force takes place at 7 P.M. and the minimum at 11 A.M.

At Bombay the maximum of northerly force takes place at 11 A.M. and the minimum at 9 P.M.; there is a very decided minimum of vertical force at 11 A.M., but there is no pronounced maximum; two minor maxima, however, occur, one at 6 A.M. and the other at midnight.

On the whole it must be said that the results of this first and praiseworthy attempt are very encouraging, and point to the supposition that the greater portion of the disturbing currents lies outside the Earth's surface.

I now come to consider another aspect of the subject. It seems quite possible to conceive a set of currents to exist in the Earth's atmosphere without exhibiting a considerable diurnal variation. Let us take, for instance, an ordinary electric circuit, say of a circular shape and horizontal, and heat it by causing some source of heat, such as a lamp, to travel slowly around it with a definite rate of progress. It will be evident that we shall have (assuming the current to be otherwise constant) no variation in flow due to this heating effect. In like manner, if there be electric currents in the atmosphere which circulate round the Earth in the direction of parallels of latitude, such currents will not be subject to a considerable solar diurnal variation. For while the conductivity of a given region would vary according to the position of the Sun with regard to it, yet the whole circuit round the Earth, which would always embrace a region affected by the Sun, would not have its total resistance altered, at least not greatly altered; and as there would be no cause for much alteration of the total electromotive force, there would be no great reason for inconstancy of current—in other words, no great solar diurnal variation.

It may, however, be asked if there are any grounds for imagining the existence of such a set of currents. To this I would reply that, assuming the existence of currents in the upper regions of the atmosphere, their disposition would certainly be to some extent subject to magneto-electric considerations. If we bear in mind the distinct connection between auroral beams and lines of magnetic force, we must certainly, I think, be prepared to admit the possibility of perhaps even a marked reference to magneto-electric considerations in the disposition of the currents in question.

For the purpose of the following argument we may consider the Earth to be at rest (*i. e.* devoid of rotation), and imagine that the Sun circulates round the equator in twenty-four hours. As a consequence of solar influence, we shall have convection-currents in the upper regions of the atmosphere flowing from the equator northwards and southwards towards the poles. Whether these currents reach the poles or come down in some intermediate region may be left an open question. Now such currents will not only be conductors, but they will form a movable system of conductors, which we may suppose to be created at the equator when they rise into the upper regions, and destroyed at the poles or those intermediate regions where they descend.

Again, for the purpose of this argument we may, without sensible error, look upon the magnetic Earth as similar to the class model that is sometimes used to represent it; that is to say, as a globe wrapped round continuously with insulated wires in the same direction which convey an electric current, the circles of such wires being small near the poles, and of course large at the equator. Now if an external insulated circuit of wire a trifle larger than the diameter of this globe be supposed to travel from the equator to either of the poles, it will leave behind more convolutions of the primary globe-current than it approaches, and will therefore be traversed by an induced current in the same direction as that of the primary; and the continuous travelling of such an external insulated system might be supposed to increase the magnetic power of the globe. Applying the same sort of reasoning to the Earth and to the convection-currents under consideration, these may be imagined to be traversed by equatorial currents, the tendency of which in both hemispheres would be to increase the general magnetism of the globe. From the reason already given such currents would have no solar-diurnal variation, but yet they would be dependent upon the state of the Sun and would vary with it. For imagine a change to take place in the radiation of our luminary producing an excess of such rays as are greedily absorbed by the upper atmospheric regions ; there would be (as I have before remarked) a sensible increase in the conductivity of these regions even if the electromotive force remained altered, and hence there would be an increase in the supposed equatorial current. In other words, such currents, while presenting no great diurnal variation, due to the carriage of a constant Sun round the Earth, would yet be eminently susceptible to any inconstancy in the sun itself. Now have we any such phenomenon connected with terrestrial magnetism? I think we have. The late John Allan Broun has, I believe, proved that we have changes in the mean daily value of the horizontal force which are simultaneous, and in the same direction at places on the Earth's surface very far removed from each other; and I have endeavoured to show that the changes of this nature recorded by him depend, as far as we can judge from somewhat imperfect records, upon the state of the Sun's surface, an increased area of spotted surface coinciding apparently with increased values of the daily means of horizontal force all over the Earth. But my chief object in giving prominence to this part of the subject is with the view of advocating that the Gaussian method of analysis should not be applied merely to the solar diurnal variations of the three magnetic elements, but that they should likewise embrace a consideration of the simultaneous variations in the mean daily values of the elements at various stations. We must, in fine, consider the possibility at least of there being in the upper atmospheric regions, not merely currents which present a solar-diurnal variation, but others that have no such variation, while yet they may be highly susceptible to changes in the Sun. The double method of treating mathematically not merely the solar-diurnal variation, but likewise the simultaneous changes in the mean daily values of the elements, would thus appear to be necessary, and sufficient for giving us the required information. Already the Greenwich scheme of publication embraces not merely information connected with the solar-diurnal variation, but gives us likewise the mean daily values of the three elements; and if a complete system of this nature be pursued by a sufficient number of well-equipped magnetical observatories, we may hope soon to obtain reasonably complete information regarding the existence and distribution of currents in the upper regions of the Earth's atmosphere.

VII. *On a Modification of* Wheatstone's *Rheostat.*

By SHELFORD BIDWELL, *M.A.**

IT is frequently desirable that the resistance of a circuit through which a current of electricity is flowing should be made to vary *continuously* and not by steps, as is necessarily the case when resistance-coils are used alone. An instrument for effecting this object was devised by Sir Charles Wheatstone in 1843, and was called by him the Rheostat. Two forms of the apparatus, both of which are well known, are described in his paper on the "Constants of the Voltaic Circuit," originally published in the Phil. Trans., and contained in the Physical Society's Reprint of Wheatstone's Scientific Memoirs.

In the first form two equal cylinders, one of wood and the other of brass, are mounted on parallel axes, and so arranged that a fine wire can be wound off the one and on to the other by turning a handle. On the wood cylinder a spiral groove is cut in which the wire lies, so that its successive convolutions are insulated from each other; but when any portion of the wire is wound upon the brass cylinder, the current passes immediately from the wire to the cylinder, and thence to one of the terminals of the instrument. The effective part of the length of the wire is therefore the variable portion which is on the wood cylinder.

In the other form there is only one cylinder, which is of wood, and has a quantity of stout wire permanently wound upon it in a spiral groove cut upon its surface. Near the cylinder and parallel to its axis is a brass rod, upon which a notched "rider," or in more modern instruments a grooved brass wheel, is capable of sliding. The notch in the rider, or the groove in the wheel, fits and presses upon the spiral wire, and when the cylinder is turned the rider or wheel moves longitudinally along the brass rod. The terminals of the instrument are connected respectively with the brass rod and with one end of the wire upon the cylinder; and the resistance introduced into the circuit depends upon the position of the point of contact of the rider or wheel with the wire.

The apparatus in either form is open to serious practical objections. In that first described it is difficult to maintain good electrical contact between the wire and the brass cylinder, both of which must be kept perfectly clean and free from dust and damp. Moreover the wire is liable to become slack and to leave its groove, and not unfrequently it breaks. In the second form there is also a difficulty in securing uniformly good contact; and if the slider fits the rod sufficiently tight, the lateral pressure upon the wire is so great that it becomes permanently stretched, and is sometimes forced completely out of its groove. The wire, too, is necessarily thick; and the whole apparatus must consequently be large and cumbersome if it is to work through any considerable range of resistance.

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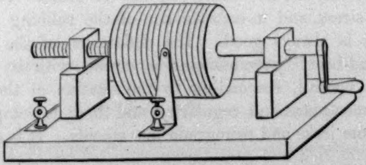
* Read May 8, 1886.

A Wheatstone's rheostat in good working order is rarely seen, even in the shop of the instrument maker; and in point of fact it is little used except for the purpose of lecture-illustration.

In the course of some experimental work the pressing need of some means of continuously varying a resistance led me to devise the modified rheostat, which is figured in the annexed woodcut.

As in the second form of Wheatstone's instrument, a wire is coiled in a spiral groove upon an insulating cylinder. This is mounted upon the middle of a brass axle of rather more than three times its length. Upon one of the projecting ends of the axle a screw is cut, the pitch of which is equal to the distance between the consecutive turns of the wire. The axle revolves in two brass bearings, fixed at a distance apart equal to twice the length of the cylinder; one of the bearings has an inside screw corresponding with that upon the axle. A flat spring is attached at one end to the base-board of the instrument midway between the bearings; to the other end is riveted a short copper pin, which is directed perpen-



dicularly to the axis of the cylinder and bears upon the spiral wire, being kept in position by a shallow notch cut in its end. One end of the spiral wire is electrically connected with the brass axle, and thence through the screwed bearing and a strip of copper with a terminal upon the base-board. The spring is directly connected with a second terminal. When the cylinder is turned by means of a handle, it travels backwards or forwards in the direction of its axis, the point of contact of the copper pin with the spiral wire remaining fixed in space; thus more or less resistance is introduced between the axle and the spring, and therefore between the two terminals.

In the model exhibited at the meeting of the Physical Society, the length of the cylinder is 3 cm., its diameter is 8 cm., and the diameter of the wire, which is of German silver, is 0·5 mm. There are nine turns of wire per centimetre of length, and the greatest resistance is about 10 ohms. Since the instrument is generally used in conjunction with a set of coils, this resistance is for most purposes amply sufficient; indeed I am inclined to think that it would be on the whole advantageous to use thicker wire and wind it in a coarser spiral, so that the total resistance might be slightly more than one ohm. The rheostat would then be used merely as a fine adjustment*.

The advantages which this apparatus appears to possess over the usual forms are obvious. It is simple, compact, easily made, and not easily put out of order. There is no lateral stress, and in consequence of the rubbing action the contact is always good. The deflections of the needle of a "dead-beat" galvanometer in circuit with it are under perfect control, responding to the rotation of the cylinder with smoothness and regularity, and there is complete freedom from jerks and retrograde movements. It is not indeed more suitable for use as a measuring instrument than the older forms; but when it is desired to adjust a resistance to a nicety, or to cause a continuous variation of a current, it is of great utility. If the interposed resistance is required to be known with accuracy, it should be measured by the bridge-method in the ordinary way.

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* The best form of cylinder would, I think, be a hollow brass drum covered with a tightly fitting tube of ebonite, 2 or 3 mm. in thickness. Wood, even when well seasoned, is liable to shrink, and is more or less affected by moisture. The depth of the groove should be about half the diameter of the wire. The wire should be annealed, and should be wound on when it is warm. The notch at the end of the copper pin may be very shallow, for if the position of the spring is properly adjusted the pin has little or no tendency to slip off the wire.

VIII. *On a Theorem relating to Curved Diffraction-gratings.*

By Walter Baily, *M.A.*[*]

In a paper read before this Society in January 1883[†], I showed that if a plane be taken perpendicular to the lines of a curved diffraction-grating, and the normal to the centre of the grating be taken as the initial line, then the equation

$$\frac{\cos^2\theta}{r}=\frac{\cos\theta}{c}+\frac{1}{d}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

in which c is the radius of curvature of the grating and d is an arbitrary constant, gives a curve having the property that if a source of light is placed at any point of the curve, the curve is the locus of the foci of all diffracted rays whether reflected or transmitted.

When d is greater than c, r may be infinite. Let ϕ be the value of θ for which r is infinite. Then

$$0=\frac{\cos\phi}{c}+\frac{1}{d},$$

and the equation to the curve may be written

$$\frac{c}{r}\cdot\cos^2\theta=\cos\theta-\cos\phi. \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

In fig. 1, G is the diffraction-grating and G N its normal; and the angle N G S is equal to ϕ. The curves marked L_1, L_2 are traced from equation (2). G S is parallel to one asymptote to the curve, so that if a source of light (say a star) is at an infinite distance on the corresponding branch of the curve it lies in the direction G S; and the foci of its diffracted light lie on the curves L_1, L_2. The foci of reflected light will lie on

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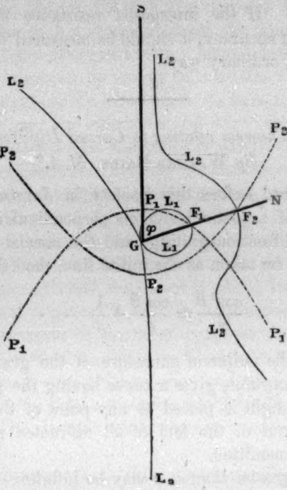
[*] Read May 8, 1886.

[†] Proceedings, vol. v. p. 181.

Fig. 1.



the oval marked L_1, and the foci of transmitted light will lie on the branches marked L_2.

Let F_1, F_2 be the points at which these curves cut the normal to the grating, and let $GF_1=\rho_1$ and $GF_2=\rho_2$. The points F_1, F_2 I will call the normal foci; F_1 is the normal focus for reflected light, and F_2 for transmitted light.

Putting $r=\rho_1$ and $\theta=0$ in (2), we have

$$c/\rho_1=1-\cos\phi; \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

and, again, putting $-r=\rho_2$ and $\theta=\pi$, we have

$$c/\rho_2=1+\cos\phi. \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

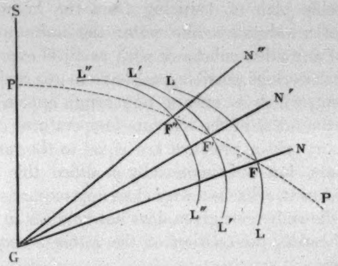
Now suppose G S the direction of the star to be kept fixed, and the grating turned so as to vary the value of ϕ; then equations (3) and (4) will give the loci of F_1 and F_2 respectively. The loci are the parabolas marked P_1 and P_2. They have a common focus G, and common axis GS, and a common latus rectum $=2c$.

F_1 is the real focus of reflected light, having a wave-length $=\frac{\sigma}{n}\sin\phi$, where σ is the distance between the lines of the grating, and n is an integer.

F_2 is the virtual focus of transmitted light having the same wave-length.

In fig. 2, P P is part of the parabola (on a larger scale)

Fig. 2.



which is the locus of the normal focus of reflected light; G N, G N′, G N″ are difference positions of the normal to the grating; and L L, L′ L′, L″ L″ are respective positions of the spectra, and F, F′, F″ are respective positions of the normal foci.

The theorem is, When the source of light is at an infinite distance the normal foci lie on two parabolas whose common focus is the centre of the grating and common latus rectum is equal to the diameter of curvature of the grating; the parabolas for reflected light being convex to the source of light, and those for transmitted light being concave.

IX. *Some Thermodynamical Relations.*—PART IV.

By WILLIAM RAMSAY, *Ph.D., and* SYDNEY YOUNG, *D.Sc.*[*]

SINCE the first portions of this research were published Professors Ayrton and Perry have criticised our work, and while we would thank them for the appreciative way in which they speak of our labours, we must differ entirely from their conclusion that "there is nothing further to be said about the four laws in question." This conclusion rests on a complete misapprehension of the whole scope of our papers, and for the obvious reason that, while we have endeavoured by a method of what may be termed approximation to arrive at a workable plan of deducing from the known vapour-pressures of a substance like water the unknown vapour-pressures of any other substance with as little expenditure of experimental work as possible, and have in our research made the statement, which is only a very rough approximation to truth, that the ratios of the absolute temperatures of any two liquids at any given pressure are equal to the ratios at any other pressure, but have materially modified this statement, and asserted next, what is a very close approximation to truth, that when the statement given does not hold (as in by far the majority of cases), the relation of the ratios is expressed by the equation

$$R' = R + c(t' - t)$$

(where R' is the ratio of the absolute temperatures of any two bodies at a given pressure; R the ratio at another pressure; t and t' the temperatures of one of the two bodies corresponding to those vapour-pressures; and c is a constant). Professors Ayrton and Perry have based all their reasoning on the first statement, which laid no claim to exactitude, and have informed us, what we already knew, that Dalton's law gives better results. The data given in our previous papers, however, show how nearly our generalization agrees with fact.

To refute the accusation of having performed useless labour would be really to repeat the substance of our previous papers; but the members of the Physical Society would hardly thank us were we to do so. There are, however, two or three remarks made by our critics which call for special reply.

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[*] Read May 8, 1886.

1. It is suggested that our obvious course would have been to employ Rankine's formula, which, our critics state, is not empirical, but based on Rankine's molecular theory. We have been informed that the formula deduced by Rankine from his molecular theory was found by him not to agree with the experimental results; and that, in order to secure agreement, an empirical term was added. We would ask if this was not the case, and, if so, whether the whole formula is not thereby rendered empirical?

2. We are told that our labours might have been reduced by 75 per cent. had we recognized the fact that our four laws are identical. Now we do not anywhere state that our "laws" are absolute, in which case only would the identity necessarily hold; but indeed give methods for calculating their deviation from constancy. It is moreover desirable to test the truth of such statements in every possible way, inasmuch as different determinations by different observers are thereby introduced.

3. That it is by no means impossible to obtain with accuracy the specific volumes of saturated vapour will appear from memoirs on the thermal behaviour of ethyl alcohol and ether, which are in the hands of the Royal Society; indeed such measurements can be made at temperatures when a direct determination of L would be extremely difficult, if not impossible. To show the necessity of using determinations from all sources, we may point out that if Regnault's values of L and of $\frac{dp}{dt}$ for alcohol and for ether are employed, and the vapour-density calculated by the thermodynamic equation

$$\frac{L}{s_1 - s_2} = \frac{dp}{dt} \cdot \frac{t}{J},$$

impossible values are obtained, unless it is supposed that chemical dissociation takes place, which is absurd.

4. We are told that the equation numbered (6) (p. 371 of the 'Proceedings'), $t = \alpha\psi(p)$, is identical with our four "laws;" and that "if (6) is true, then it follows that the ratio of the absolute temperatures of two vapours to one another at

any pressure is the same as at any other pressure, or $\theta = \kappa t$ (7). In fact, then, we can test laws I., II., III., and IV. by simply testing (7); and as we find from Regnault and Rankine's formula that (7) is untrue, there is nothing further to be said about the four laws in question." We hope that no one has, like Professors Ayrton and Perry, so misunderstood our papers as to suppose that we imagine that "the ratio of the temperatures of two vapours at any pressure is always the same as at any other pressure." We do, indeed, notice that this statement holds with very close approximation for like bodies, such as chloro- and bromo-benzene; but the whole of the second and third parts of our memoir are devoted to an attempt, which we deem not unsuccessful, to give a method whereby the *deviation from the above statement can be estimated.*

The didactic remarks so kindly directed to us at the beginning of Messrs. Ayrton and Perry's critique, lead us to suppose that the great importance of such problems in Chemistry is not so generally known as we had imagined; and we would cordially agree that the cooperative principle may here with advantage be applied, and physicist and chemist mutually assist each other.

The problem of dissociation has for long invited the attention of chemists. Many compounds decompose at a moderately high temperature, and their constituents reunite when the temperature is lowered. It is argued that, were it possible to attain a sufficiently high temperature, all the simpler compounds at least would exhibit the phenomena of dissociation.

From the nature of gases, it is to be expected that a study of the behaviour of dissociating gases would be the simplest way of arriving at a knowledge of the subject. An obvious criterion of the amount of dissociation is given by the vapour-density of the partially dissociated body; for if the dissociating gas, and the simpler gases resulting from its dissociation, obey Boyle's and Gay-Lussac's laws, then it is easy to calculate from the density of the gas the percentage number of molecules decomposed. But there is no means of knowing whether the dissociating substance, as such, does or does not obey these laws; hence it is evidently desirable to ascertain the behaviour of substances which do not dissociate as regards expansion and compressibility; so that some idea may be gained as to the influence exerted by molecular attraction between like molecules on the volume they occupy. An investigation of this nature is best carried out by ascertaining the behaviour of gases when they are becoming increasingly subject to molecular attraction, *i. e.* when they are approaching the condition of saturated vapours. The pressure of saturation is, under normal circumstances, identical with the vapour-pressure; hence the importance of a knowledge of this quantity. We have before remarked, that we have communicated to the Royal Society the results of experiments on alcohol and ether with this view.

Again, if the body exerting vapour-pressure be one capable of partial dissociation on passage from the solid or liquid to the gaseous state, its apparent vapour-pressure will really consist of its real vapour-pressure, and also of the pressure due to its dissociation into its constituents. It is evidently of importance to determine the latter independently of the former; and it is only by the employment of some law applicable to all bodies, and deduced from the behaviour of stable substances, that an idea can be formed of the pressure due to the second cause.

In the Philosophical Magazine for April 1886, p. 299 (*ante*, p. 22), Professor Unwin also comments on our papers, and, unlike Professors Ayrton and Perry, has appreciated our motive in bringing forward the subject. We have to thank him for pointing out the relation of the ratio of the total heat of vaporization to the heat expended in external work, deduced from the second half of the thermodynamic equation. We agree with him that the approximate constancy there observed lies at the basis of all the relations found by us.

We have taken the liberty of applying his formula

$$\frac{t^{n+1}}{p} \times \frac{dp}{dt}$$

to alcohol, ether, and mercury, using the vapour-pressures determined by us over a wide range of temperatures in the first two cases; and for mercury, the results given in the Journ. Chem. Soc. 1886, p. 37.

We have taken the value of $(n+1)$ for alcohol as 2·248, for ether as 2·23, and for mercury as 2·21.

The values of the expression $\frac{t^{n+1}}{p} \cdot \frac{dp}{dt}$ at different pressures are as follows:—

Alcohol.				Ether.			
Press. millim.	Temp. abs.	$\frac{dp}{dt}$.	$\frac{t^{2 \cdot 248}}{p} \cdot \frac{dp}{dt}$.	Press. millim.	Temp. abs.	$\frac{dp}{dt}$.	$\frac{t^{2 \cdot 23}}{p} \cdot \frac{dp}{dt}$.
23·733	283	1·516	20700	184·9	273	8·843	12950
540·91	343	22·750	20376	921·18	313	31·16	12393
1692·3	373	58·175	20721	2293·9	343	62·84	12341
2359·8	383	75·95	20592	7495·7	393	153·95	12156
5686·6	413	151·75	20226	13281	423	234·9	12715
14764	453	315·45	19931	21804	453	336·4	12921
22182	473	430·8	19966				
45519	513	763·7	20703				

Mercury.

Pressures, millim.	Temp. abs.	$\frac{dp}{dt}$.	$\frac{t^{2 \cdot 21}}{dt} \cdot \frac{dp}{dt}$.
10·0	457·30	0·350	26486
100·0	534·20	2·506	26743
200·0	563·44	4·470	26833
500·0	608·03	9·40	26703
1000·0	647·20	16·37	26697
3000·0	723·10	38·61	26811
5000·0	765·60	56·90	26904

With mercury, the value of n is much more nearly constant than if Regnault's numbers be employed.

It will be noticed that this number is much higher than that given by Professor Unwin (0·69, while ours is 1·21); but it is worthy of remark, that if the values of n be calculated for the stable substances mentioned in our first paper, taking the highest and lowest pressures, and the corresponding values of $\frac{dp}{dt}$, the value of n varies between the narrow limits 1·15 and 1·52. Although we have not verified these values for intermediate pressures except in the examples already given, it may be of interest to reproduce them.

Substance.	Pressures from which n was calculated.	Value of n.
Carbon disulphide . . .	50 and 5000	1·147
Ethyl bromide	50 and 5000	1·316
Ethyl chloride	50 and 5000	1·243
Carbon tetrachloride . .	50 and 5000	1·326
Bromobenzene	50 and 800	1·475
Chlorobenzene	100 and 700	1·480
Chloroform	200 and 5000	1·376
Ethylene	10 and 400	1·235
Sulphur	300 and 3000	1·251
Bromo-naphthalene . .	150 and 800	1·196
Methyl salicylate . . .	50 and 800	1·517
Aniline	50 and 800	1·218
Methyl alcohol	50 and 5000	1·395

It was found impossible to obtain a constant value for n with dissociating substances when different pressures were employed.

The whole subject of vapour-pressure is one that cannot well be considered on its own merits, for they must evidently be intimately related to other physical properties; and although we have already accumulated data for alcohol and ether bearing on this subject, we prefer to reserve a general consideration of the question until an investigation, as regards the thermal behaviour of other bodies, on which we are at present engaged, shall have been finished.

X. *Some Thermodynamical Relations.*—Part V.

By William Ramsay, *Ph.D.*, *and* Sydney Young, *D.Sc.**

In the first two of the series of papers on "Some Thermodynamical Relations," published in the previous volume of the 'Proceedings' (vol. vii.), it was shown by one of us that the ratio of the absolute temperatures of nearly related bodies, such as chlorobenzene and bromobenzene, or ethyl chloride and ethyl bromide, is constant for equal vapour-pressures; and that a relation exists between the ratios of the absolute temperatures of all bodies which may be expressed

* Read May 22, 1886.

by the equation

$$R' = R + c(t' - t),$$

where R is the ratio of the absolute temperatures of the two bodies corresponding to any vapour-pressure, the same for both; R′ is the ratio at any other vapour-pressure, again the same for both; c is a constant which may be 0 or a small + or − number; and t' and t are the temperatures of one of the two bodies corresponding to the two vapour-pressures.

The determination of the vapour-pressures of a large series of compound ethers by Schumann (Wiedemann's *Annalen*, 1881, p. 40) affords an opportunity of studying the relations of a great number of bodies of the same type; and it appears that in this case also the ratio of the absolute temperatures of any two of the ethers is a constant at all pressures. The following table shows the ratios of the absolute temperatures of all the ethers

Ratios of Absolute Temperatures of Ethers to those of Ethyl Acetate at definite Pressures.

Ether.	Pressure.			Mean.
	1300 millim.	760 millim.	200 millim.	
Methyl formate	·8715	·8720	·8706	·8714
Ethyl formate	·9344	·9352	·9323	·9340
Propyl formate	1·0109	1·0111	1·0115	1·0112
Isobutyl formate	1·0585	1·0594	1·0573	1·0584
Amyl formate	1·1345	1·1320	1·1329	1·1331
Methyl acetate	·9420	·9440	·9431	1·9430
Propyl acetate	1·0678	1·0677	1·0690	1·0682
Isobutyl acetate	1·1122	1·1120	1·1120	1·1121
Methyl propionate	1·0073	1·0080	1·0073	1·0075
Ethyl propionate	1·0615	1·0605	1·0614	1·0611
Propyl propionate	1·1290	1·1288	1·1291	1·1290
Isobutyl propionate	1·1704	1·1705	1·1705	1·1705
Amyl propionate	1·2366	1·2374	1·2401	1·2380
Methyl butyrate	1·0724	1·0720	1·0716	1·0720
Ethyl butyrate	1·1220	1·1223	1·1202	1·1215
Propyl butyrate	1·1889	1·1874	1·1902	1·1888
Isobutyl butyrate	1·2279	1·2279	1·2278	1·2279
Amyl butyrate	1·2905	1·2899	1·2901	1·2902
Methyl isobutyrate	1·0444	1·0434	1·0433	1·0437
Ethyl isobutyrate	1·0953	1·0943	1·0935	1·0944
Propyl isobutyrate	1·1604	1·1623	1·1609	1·1612
Isobutyl isobutyrate	1·2001	1·1985	1·1985	1·1990
Amyl isobutyrate	1·2644	1·2619	1·2637	1·2633
Methyl valerate	1·1135	1·1131	1·1139	1·1135
Ethyl valerate	1·1642	1·1634	1·1619	1·1632
Propyl valerate	1·2257	1·2251	1·2265	1·2258
Isobutyl valerate	1·2635	1·2617	1·2634	1·2629

to those of ethyl acetate at pressures of 200, 760, and 1300 millims. (The boiling-points at these pressures are given by Schumann.) It will be seen that in every case the ratio is very nearly constant at each pressure; and the deviations from constancy may well be due to the great difficulty of obtaining perfectly pure specimens, evidenced by the fact that only one ether boiled with perfect constancy, the rise of temperature during distillation amounting in one case to 0°·7, while the average rise was 0°·37. The absolute temperatures of ethyl acetate corresponding to 1300, 760, and 200 millim. are 367°·3, 350°·1, and 314°·4.

Taking the mean ratio for each ether, and the temperatures of ethyl acetate at the three pressures as correct, the boiling-point of the ethers were recalculated; and the following table contains these values, together with the observed temperatures and the differences between the observed and calculated temperatures:—

Absolute Temperatures.

Ether.	Observed.			Calculated.			Differences.		
	1300 mm.	760 mm.	200 mm.	1300 mm.	760 mm.	200 mm.	1300 mm.	760 mm.	200 mm.
Methyl formate......	320·1	305·3	273·7	320·1	305·1	274·0	0	−0·2	+0·3
Ethyl formate	343·2	327·4	293·1	343·1	327·0	293·6	−0·1	−0·4	+0·5
Propyl formate	371·3	354·0	318·0	371·4	354·0	317·9	+0·1	0	−0·1
Isobutyl formate ...	388·8	370·9	332·4	388·7	370·5	332·8	−0·1	−0·4	+0·4
Amyl formate	416·7	396·3	356·2	416·2	396·7	356·2	−0·5	+0·4	0
Methyl acetate	346·0	330·5	296·5	346·4	330·0	296·5	+0·4	−0·5	0
Propyl acetate	392·2	373·8	336·1	392·3	374·0	335·8	+0·1	+0·2	−0·3
Isobutyl acetate ...	408·5	389·3	349·6	408·5	389·3	349·6	0	0	0
Methyl propionate ..	370·0	352·9	316·7	370·1	352·7	316·8	+0·1	−0·2	+0·1
Ethyl propionate ...	389·9	371·3	333·7	389·7	371·5	333·6	−0·2	+0·2	−0·1
Propyl propionate...	414·7	395·2	355·0	414·7	395·3	355·0	0	+0·1	0
Isobutyl propionate	429·9	409·8	368·0	429·9	409·8	368·0	0	0	0
Amyl propionate ...	454·2	433·2	389·9	454·7	433·4	389·2	+0·5	+0·2	−0·7
Methyl butyrate ...	393·9	375·3	336·9	393·7	375·3	337·0	−0·2	0	+0·1
Ethyl butyrate	412·1	392·9	352·2	411·9	392·6	352·6	−0·2	−0·3	+0·4
Propyl butyrate ...	436·7	415·7	374·2	436·6	416·2	373·8	−0·1	+0·5	−0·4
Isobutyl butyrate ...	451·0	429·9	386·0	451·0	429·9	386·0	0	0	0
Amyl butyrate	474·0	451·6	405·6	473·9	451·7	405·6	−0·1	+0·1	0
Methyl isobutyrate..	383·6	365·3	328·0	383·4	365·4	328·1	−0·2	+0·1	+0·1
Ethyl isobutyrate ...	402·3	383·1	344·1	402·0	383·2	344·1	−0·3	+0·1	0
Propyl isobutyrate ..	426·2	406·9	365·0	426·5	406·5	365·1	+0·3	−0·4	+0·1
Isobutyl isobutyrate	440·8	419·6	376·8	440·4	419·8	377·0	−0·4	+0·2	+0·2
Amyl isobutyrate ...	464·4	441·8	397·3	464·0	442·3	397·2	−0·4	+0·5	−0·1
Methyl valerate......	409·0	389·7	350·2	409·0	389·8	350·1	0	+0·1	−0·1
Ethyl valerate	427·6	407·3	365·3	427·2	407·2	365·7	−0·4	−0·1	+0·4
Propyl valerate......	450·2	428·9	385·6	450·2	429·2	385·4	0	+0·3	−0·2
Isobutyl valerate ...	464·1	441·7	397·2	463·9	442·1	397·1	0·2	+0·4	−0·1

It will be noticed that the greatest difference between the observed and recalculated temperatures is $0^\circ\cdot7$, which is probably within the limits of experimental error, for the reason already stated. If this is so, the equation $\frac{t_2'}{t_1'}=\frac{t_2}{t_1}$ holds good for this series of ethers, where t_2' and t_2 are the absolute temperatures of any one of the ethers corresponding to two vapour-pressures, and t_1' and t_1 the absolute temperatures of any other ether at the same pressures. If the ethers are compared with some other substance, such as water, the equation

$$\frac{t_1'}{\mathrm{T}'}=\frac{t_1}{\mathrm{T}}+c(\mathrm{T}'-\mathrm{T})$$

must be employed, where t_1' and t_1 are the absolute temperatures of the ether, and T′ and T those of water at any two pressures. If the left side of this equation be multiplied by $\frac{t_2'}{t_1'}$ and the right by $\frac{t_2}{t_1}$, $\frac{t_2'}{t_1'}$ being equal to $\frac{t_2}{t_1}$, the equation becomes

$$\frac{t_2'}{\mathrm{T}'}=\frac{t_2}{t_1}\left\{\frac{t_1}{\mathrm{T}}+c(\mathrm{T}'-\mathrm{T})\right\}$$

$$=\frac{t_2}{\mathrm{T}}+c\frac{t_2}{t_1}(\mathrm{T}'-\mathrm{T}).$$

That is to say, if the members of this series of ethers be compared with water, both the ratios at any given pressure, corresponding to t_1, t_2, &c. and the constant c vary directly as the boiling-points (absolute) of the ethers at that pressure.

Taking the boiling-point of ethyl acetate at the normal pressure to be correct, and the ratio of the absolute temperature of ethyl acetate to that of water at that pressure therefore to be $\frac{350\cdot1}{373\cdot0}=0\cdot9386$, and the value of c to be $0\cdot000387$, the ratio of the absolute temperature of ethyl acetate to that of water at any other pressure is given by the equation

$$\frac{t'}{\mathrm{T}'}=0\cdot9386+0\cdot000387\,(\mathrm{T}'-373),$$

where t' is the absolute temperature of ethyl acetate, and T′ that of water.

The calculated and observed temperatures are :—

Pressure.	Temperature.	
	Observed.	Calculated.
1300	367·3	367·2
200	314·4	314·4

For any other ether in the series the equation is

$$\frac{t'}{T'} = \frac{t}{350{\cdot}1} \{0{\cdot}9386 + 0{\cdot}000387\ (T' - 373)\},$$

where t is the boiling-point of the ether at constant pressure.

For pressures of 1300 and 200 millim. respectively the equation becomes simply

$$t' = 1{\cdot}0488t$$

and

$$t' = 0{\cdot}89795t.$$

It appears therefore that by determining simply the boiling-point of an ether belonging to this type, and knowing the vapour-pressures of water (or of one of the other ethers), it is possible to calculate the temperatures corresponding to any other pressure, at any rate between the limits of 200 and 1300 millim.

PROCEEDINGS

OF

THE PHYSICAL SOCIETY

OF LONDON.

AUGUST 1886.

XI. *On a new Hyperbolagraph.* *By* H. CUNYNGHAME*.

It is a not unfrequent want to be able to find the rectangle of greatest or least area contained between a curve and any given rectangular coordinate axes. In several problems connected with motion and pressure in steam-engines this is very useful; and even in political economy the graphic representations of monopoly-curves depend on the maxima and minima of this nature.

For the solutions of such problems it is often very useful to be able to describe any rectangular hyperbola, the axes being given. To effect this, I have constructed a machine which is capable of drawing these curves with considerable accuracy. It depends on a mathematical property of the rectangular hyperbola, which, so far as I am aware, is new. From a fixed point O let a line O P be drawn to meet a fixed line A B in P. Take P Q perpendicular to A B, and make O P + P Q = a constant length. Then the locus of Q is a rectangular hyperbola whose asymptotes are equally inclined to A B, and such that if the said asymptotes be taken as axes, $xy = 2(\mathrm{OM})^2$. This is easy to prove; for if $\mathrm{PM} = x$, $\mathrm{PQ} = y$, and $\mathrm{OQ} = b$ and

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* Read June 12, 1886.

$OM=b$; then

$$y=a-OP,$$

$$=a-\sqrt{b^2+x^2},$$

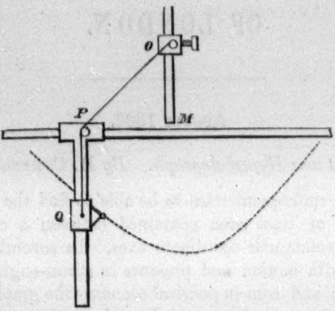
or

$$a^2-2ay+y^2=b^2+x^2,$$

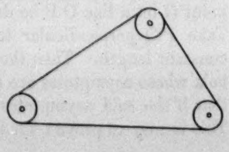
$$x^2-y^2+2ay=a^2-b^2,$$

which is the equation to a rectangular hyperbola.

The line O P Q, instead of being made of thread, is made of a fine wire of steel wound round a roller at O, and given one complete turn round the roller at P, fixed to the movable T-square P Q. It is kept stretched by means of a string and weight, or a spring pulling it away (not shown in the figure).



This use of rollers and a fine steel wire, or a band, is very useful in all instruments depending on the use of strings. As a substitute for it, a flat band of steel or copper wire may sometimes also be employed. It will of course be noticed that the rollers form a compensation arrangement, for as much as is rolled on to one roller is rolled off the other. It will also not fail to be noticed, that an elliptograph could be constructed in this manner by the use of a steel wire and rollers; the rollers



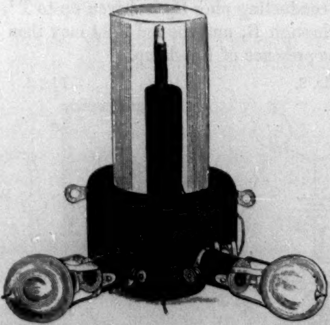
being arranged so as to compensate one another, so that when much wire was rolled up on one, less would be rolled up on the others. This principle has hardly been sufficiently used up to now, and is worthy of attention. In many other instruments depending on the length of strings, the direction of the forces altering, there is unequal strain; but in this instrument (as was pointed out by Mr. Boys) there will be no such tendency, as the string is always kept stretched by a constant weight.

XII. *On an Electric-light Fire-damp Indicator.*

By Walter Emmott *and* William Ackroyd *.

The Royal Commission on Accidents in Mines point out, in their recently issued Report, a serious objection to the use of the electric light in mines, notwithstanding its many other great advantages, in that the light of an incandescent lamp being produced within a vacuum cannot admit of any device for the indication of fire-damp such as is employed in the Davy for example. This difficulty was experienced by one of us in the course of an installation of the electric light in the Lofthouse pit, Wyke, Yorks, in the summer of 1885; and we have since made a series of experi-

Fig. 1.



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* Read June 12, 1886.

ments with the object of devising a method of making the electric light an indicator of fire-damp. The apparatus placed before the Physical Society is the outcome of our work. It consists of two incandescent lamps, one with white glass and the other with red, and other necessary adjuncts, such that in an ordinary atmosphere the white incandescent lamp alone shines, but in fire-damp the white lamp goes out and the red one begins to emit its light. This is effected as follows :—A porous pot of unglazed hard-baked porcelain is joined by air-tight connections to a tube a portion of which is represented by $T\,T^1$, fig. 2. This tube is of such an internal diameter that it will readily admit of being sealed with a small quantity of mercury, H*g*. A platinum wire runs the whole length of the tube and is connected with one of the poles of the battery B or other source of electricity. Two other platinum wires in the tube run parallel with this for part of the way, as in fig. 2, and each is connected with a lamp. The lamps W and R are joined, and a branch wire connects them to the other pole of the battery. In fig. 2 the current is represented as flowing through W ; when from diffusion in an atmosphere of fire-damp, the conducting plug H*g* is driven up to T^1, the current will flow through R, and the red light may then be taken to indicate the presence of fire-damp.

Fig. 2.

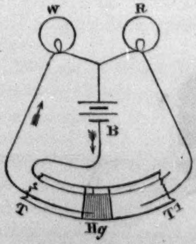
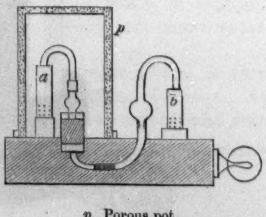


Fig. 3.



p. Porous pot.
a and *b*, desiccating tubes.

The wires being within the tube, one or other of the lamps must always be shining so long as there is a current, whether the apparatus be in an atmosphere of fire-damp, choke-damp, or air ; and to prevent the mercury being driven out of the tube by too much pressure, bulbs are arranged on either side as in fig. 3, which presents a diagrammatic view of the apparatus. We have found an internal diameter of tubing of about 3 millim. best adapted for ensuring easy mobility of the mercury. The presence of the wires within the tube has interfered with the perfection of the seal; this we have overcome by the introduction of a little concentrated sulphuric acid, which also serves the purpose of preventing sparking and of lubricating the interior. The use of sulphuric acid necessitates the addition of desiccators *a* and *b*, fig. 3, to each end of the tube; but in cases where it has been found advisable not to use sulphuric acid, both the acid and the desiccators have been dispensed with by slightly modifying the arrangement of the wires at the lower part of the tube. With this form of apparatus we are readily able to detect the presence of 5 per cent. of coal-gas in a mixture of this gas with air; and with a mercury seal of less weight and closer proximity of the wires at T and T^1 (fig. 2), it appears possible to get any required degree of sensitiveness. It is proposed to have the apparatus fixed in the main roads and hauling roads in pit installations.

DR. H. SPRENGEL exhibited at the meeting on May 22 the following objects connected with the Hell-Gate Explosion near New York; viz.:—

(1) Three photographs taken of the Flood Rock from three different points at the moment after the explosion, October 10, 1885, when the mine was charged with 22 tons of dynamite and 107 tons of one of Dr. Sprengel's Safety-Explosives (Journ. Chem. Soc. 1873, p. 806).

(2) A sample of this Safety-Explosive (79 per cent. potassium chlorate and 21 per cent. nitrobenzene), possessing the power 109 according to General Abbot, U.S. Army (dynamite with 75 per cent. nitroglycerin being 100).

(3) Effects on lead, produced by the explosion of equal weights of another series of Safety-Explosives—the Nitric-Peroxide mixtures—demonstrating their greatly superior power over that of nitroglycerin.

XIII. *Note on a Mode of maintaining Tuning-Forks by Electricity.* *By* Prof. S. P. Thompson*.

All who have worked with self-maintained electric tuning-forks have met with the fact that these instruments as ordinarily arranged give a very irregular note, the pitch of which is continually slightly altering, and even those which are fairly constant in pitch are continually changing the phase of their vibrations. These changes of phase and of pitch render the electrically-sustained tuning-fork as usually constructed almost useless for acoustic work, and diminish the usefulness of the instrument for chronoscopic and electric applications. They appear to be due to a fact which is tolerably obvious to any one acquainted with the fundamental principles of the vibrations of elastic bodies, namely, that the impetus given by the electromagnet at each vibration is given at the wrong instant of the motion, namely at some other instant than that during which the fork is passing with maximum velocity through the position of zero displacement. In the older forms of electro-diapason constructed by Fessel and by Koenig†, the electromagnet was of horseshoe form, having poles outside the prongs of the fork; whilst in the more recent instruments by Koenig the electromagnet is of short cylindrical form, and placed between the prongs of the fork. The latter arrangement, which is preferable for several reasons electrical and mechanical, seems to have been first suggested by Lord Rayleigh‡. In the earlier form contact was made by a stylus, carried by the prong of the fork, dipping into the mercury cup: in the later form the stylus usually makes contact against a platinum-headed screw, almost exactly as does the interrupter of Wagner so common in electric bells. In either case contact is made at a very brief interval before the prong of the fork reaches its extreme elongation away from the pole of the electromagnet, and is broken at a slightly longer interval after the prong has passed its extreme elongation, the difference arising from the elasticity of the stylus, and the necessary imperfection of the contact until a certain actual contact-pressure has been attained. There is also a certain retardation in the electro-magnetic pull behind the instant of greatest current, owing to the self-induction of the circuit and the mutual induction between the coil and its core. But if the core be short, and laminated, and of good iron, and if the resistance of the circuit be considerable in proportion to its coefficient of self-induction, the retardation of phase in the periodic electromagnetic impulses will not be of any great importance. Lord Rayleigh remarks* that if the magnetic force depended only on the position of the fork the phase might be considered to be 180° in advance of that of the fork's own vibration. That is to say, considering a displacement of the fork toward the electromagnet positive, the maximum force occurs when the displacement is a negative maximum. But, adds Lord Rayleigh, the retardation due to self-induction and imperfect contact reduces this advance. Lord Rayleigh further remarks that if the phase-difference be reduced to 90° the force acts in the most favourable manner, and the greatest possible vibration is produced. He might have added that in this case the tendency to produce phase-change is the least possible. He suggested as a means of producing any desired retardation, the use of a stylus attached not to the prong itself, but to the further end of a light straight spring carried by the fork.

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* Read June 26, 1886.

† *Vide* Helmholtz, 'Sensations of Tone,' Ellis's edition of 1875, p. 178.

‡ 'Theory of Sound,' vol. i. p. 56.

It seems to the present writer, that a better way to secure the proper timing of the impulses is to be found in the suggestion which he now makes, and which arose in his mind after considering the difference of phase which exists between two dynamo-electric machines associated together. Let two forks in unison with one another be provided, and let each act as interrupter to the other, but not to itself; the electromagnet of each being included in the circuit of the other's contact-points. One battery will suffice for the two, as they will not both make contact at the same time.

Fig. 1 shows the proposed arrangement. The forks when started will settle down to a difference of phase corresponding to an almost exact quarter of a period.

Fork B is arranged, as shown in fig. 1, so that it makes contact at the inward stroke at the point when its displacement is at the positive maximum ; fork A makes its contact at the outward stroke when its displacement is at the negative maximum.

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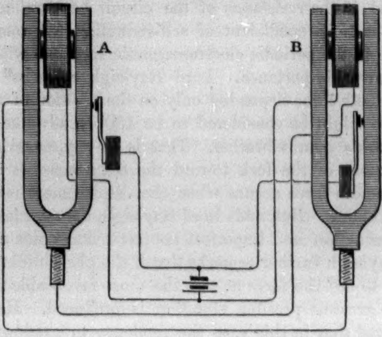
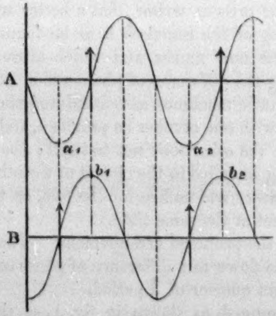
* *Op. cit.* p. 59.

Fig. 1.



Reference to figure 2 will elucidate the phase relations. In this figure the upper curve relates to fork A and the lower

Fig. 2.



to fork B. Positive values of the ordinates relate to positive displacements in the sense of approach to the electromagnet.

When A has moved through ¼ of its cycle of movements, and the displacement is a negative maximum a_1, it makes contact for B's electromagnet, which gives a momentary impulse just as B has phase 0°. A quarter of a period later B makes contact (b_1), and gives an impulse to A just when A's phase is 0°. The arrows indicate the instant and direction of the forces. It is assumed that the retardation due to self-induction is small, as compared with the period of the forks; and this may easily be made so, firstly, by employing only short internal electromagnets with laminated cores, and, secondly, by interposing sufficient inductionless resistance in the circuit.

Another point of some importance in the construction of electrically sustained forks is that the contacts should be very firm, and should be made much nearer the hilt of the fork than is usual in these instruments. When the stylus is near the outward end of the prong there is much greater amplitude of motion at the contact than is really requisite. A pin of platinum secured to the prong at about 5 centimetres from the point of bifurcation, making contact against a platinum-faced strip of German silver, half a millimetre in thickness, to serve as a spring, will answer the purpose for forks of ordinary size.

A common imperfection in the electro-diapason as usually constructed is the method of mounting the fork. Its shank is held with nut and washer to a block of wood or metal, which is then secured to a stand by a single bolt or screw which runs at right angles to the shank and to the planes of vibration of the prongs. The defect of this mounting is that the fork can shift a little round the bolt, and is liable to become set with one prong nearer one face of the electromagnet than the other prong is to the other face. This often results in the occurrence of actual rattling contacts between the fork and the electromagnet, as well as in derangements of the adjustment of the working contacts. It also gives rise to another kind of difficulty: if one prong is nearer to the electromagnet than the other is, there will be a tendency for the fork to vibrate as a whole around the bolt or frame upon which it is mounted, and this will give rise to slow alternations of good and bad contacts, producing on the sound an effect not unlike that of beats. Either the bolt which secures the fork to its mounting should lie in the plane of the vibrations, or else it should be replaced by a more substantial species of mounting.

XIV. *Further Notes on the Formulæ of the Electromagnet and the Equations of the Dynamo.* *By* Professor SILVANUS P. THOMPSON, *D.Sc., B.A.*[*]

1 *The Lamont-Frölich Formula.*

DR. O. FRÖLICH has done me the honour of replying[†] to a certain point in my former communication to the Physical Society, "On the Law of the Electromagnet and the Law of the Dynamo"[‡]. In that communication I pointed out that Lamont had in 1867 published a rational theory of the electromagnet, based upon the assumption that the permeability of the iron was at every stage of the magnetization proportional to the deficit of saturation, leading him to an exponential expression,

$$m = M(1 - \epsilon^{-kx}),$$

where m is the magnetism present at any stage, M its maximum value, k the ratio of the permeability to the deficit of saturation, and x the magnetizing force proportional (approximately) to the number of ampere-turns of the magnetizing current. This formula more correctly expressed the facts than either of the commoner formulæ of Lenz and Jacobi and of Müller.

I further pointed out that Lamont had himself[§] given, as a sufficient approximation to the formula, the simpler expression,

$$m = \frac{aMx}{M + ax},$$

which formula is mathematically identical with that now commonly attributed to Dr. Frölich. For, writing $a = kM$, we get at once

$$m = M\frac{kx}{1 + kx},$$

which is the formula claimed by Frölich.

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[*] Read June 26, 1886.

[†] *Elektrotechnische Zeitschrift*, vii. p. 163, May 1886.

[‡] Proceedings, vol. vii. p. 265.

[§] Lamont, *Magnetismus*, p. 41.

Lamont having developed his exponential expression in a series of ascending powers of kx, I did the same for the simpler formula for the purpose of comparison, and showed that, *neglecting the fourth and higher terms* of each series, the expansions are very nearly equal for all values of kx except for very large ones, and are identical for the value $kx=\frac{3}{5}$. Dr. Frölich, overlooking the words I have above italicized, commits the mistake of supposing that I had said that Lamont's exponential expression is identical in value with the simpler formula when $kx=\frac{3}{5}$. I have said nothing of the kind.

Further, when Dr. Frölich says, " Hiernach ist die Aussicht vorhanden dass nicht die Lamontsche sondern die von mir benutzte Formel die wahre Gesetz der Elektromagnete enthält," he is forgetting that the formula used by him is also Lamont's. He has proved, in his most recent communication, that the differences between the calculated and the observed values are about half as great when calculated by the simpler formula. The second and simpler formula suggested by Lamont appears therefore to be better than the first and more complex formula which he suggested. It has been recently shown by Mr. Bosanquet[*] that if we take as expressive of the permeability, not the instantaneous value dm/dx, but the integral value m/x, and treat this on Lamont's plan as proportional to the deficit of saturation,

$$\frac{m}{x}=k(\mathrm{M}-m),$$

we deduce at once the formula in question. Dr. Frölich's researches upon the dynamo have given us the most complete and perfect proofs of the adequacy of the formula to represent the facts of the electromagnet as it is used in practice. My former communication was indeed mainly written to point out the extreme value and interest of Dr. Frölich's work from this point of view.

2. *Frölich's simplified Formula of the Electromagnet.*

Since my former communication to the Physical Society was made, a further work on the theory of the dynamo by

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[*] 'Electrician,' vol. xvi. p. 247, February 1886.

Dr. Frölich has appeared*. In this work he carries the simplification of the formulæ of magnet and of dynamo one stage further by introducing considerations somewhat closely connected with those which entered into my own work of 1883–4.

The form adopted by me in 1883 for the Lamont-Frölich formula was

$$H=\frac{G\kappa Si}{1+\sigma Si};$$

where H is the resulting average intensity of the magnetic field (in which the armature rotates), κ the initial value of the magnetic permeability, G a coefficient depending upon such purely geometrical quantities as the form and size of core, pole-pieces, and coils, S the number of windings of the magnetizing coil, and σ the "saturation-coefficient." This can be transformed at once to Frölich's form by writing $M=G\kappa/\sigma$; $k=\sigma$; $x=Si$. In 1884 I pointed out† the nature of this saturation-constant and its importance in the resulting equations of the dynamo. It is the reciprocal of that number of ampere-turns which, to mark its importance, I ventured to term "diacritical," namely *that number of ampere-turns which will reduce the instantaneous value of the magnetic permeability to half its initial value*, or which, in the formula used, will give to the magnet exactly *half its maximum magnetism.* I further pointed out in my lectures on the dynamo that year, that, if the number of windings of the coil S is given, there will be a "diacritical" current, namely a particular value of current which will exactly half-saturate the magnet. Dr. Frölich has independently made use of this conception, and has applied it to the formula of the electromagnet. The argument is his, but I retain the notation I have used.

Writing $(Si)'$ for the diacritical number of ampere-turns, we have (as I showed in 1884) $(Si)'=1/\sigma$.

Taking the expression

$$H=\frac{G\kappa Si}{1+\sigma Si}=\frac{G\kappa}{\sigma}\cdot\frac{Si}{\frac{1}{\sigma}+Si},$$

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[*] *Die dynamoelektrische Maschine. Eine physikalische Beschreibung für den technischen Gebrauch*, von Dr. O. Frölich (Berlin, 1886).

[†] 'Dynamoelectric Machinery,' first edition, p. 221; also Report Brit. Assoc., Montreal Meeting, 1884.

and writing

$$Y=\frac{G\kappa}{\sigma},$$

we have

$$H=Y\frac{Si}{Si+(Si)'},$$

where Y is obviously the limiting maximum value of H when the excitement is infinitely great. If S is given, then i' is the diacritical current, and the expression becomes

$$H=Y\frac{i}{i+i'},$$

which is true for every electromagnet excited by a single current. Two observations made on any electromagnet will determine the two constants Y and i'. Further, if r be the resistance of the magnetizing coil, since $ir=e$ (the potential requisite to send the current through the coil), we may obviously write the equation

$$H=Y\frac{e}{e+e'};$$

where e' is the diacritical difference of potential, namely that difference of potential which, applied to the coil of resistance r and of S convolutions, will half-saturate the core.

The extreme convenience of this form of the law of the electromagnet must be at once apparent, since it enables the equation of a given magnet to be instantly adapted to the case of any given current or potential, and is equally applicable to express either the intensity of the field or the magnetic moment of the magnet. To put the matter in a more general way, let ψ represent current, or potential, or ampere-turns, and let ψ' be the diacritical value of the same for the given magnet; let ϕ be the intensity of the field, or the strength of the pole, or the magnetic moment, or the integral of the magnetic induction, and Φ its maximum value; then

$$\phi=\Phi\frac{\psi}{\psi+\psi'}.$$

This being the general equation of the electromagnet, it remains to be shown how excessively simple become the equations of the various kinds of dynamo.

3. *Equations of the Series-wound Dynamo.*

If A is the "equivalent area" of the coils of the armature, and H the average strength of the field in which it turns, the number of lines of force cut in each quadrant is AH; hence the average electromotive force at the speed n is

$$E = 4nAH. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

But

$$H = Y\frac{i}{i+i'},$$

and, writing $B = 4AY$, and remembering that, if ΣR be the sum of the resistances in the circuit, $E/\Sigma R = i$ (by Ohm's law), we get

$$i = \frac{nB}{\Sigma R} - i'.$$

But Y being the maximum value of H, it is obvious that nB is the maximum value that E could possibly have (at that speed) even if the magnets were separately excited to saturation. Hence $nB/\Sigma R$ is the maximum value that i could have if the magnets were thus separately saturated and the armature, driven at speed n, were in a circuit the total resistance of which was equal to ΣR. Adopting Frölich's notation here, we will write as $\bar{i}$ this current; and as it is important to distinguish the current generated under such conditions, I propose to call it the "maximal" current*. The equation of the series dynamo now becomes

$$i = \bar{i} - i'; \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

or, multiplying each term by ΣR,

$$E = \bar{E} - E', \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where $\bar{E}$ is the "maximal" value of E at that speed with saturated magnets. And, again, writing e for the difference of potentials at the terminals of the machine, since e, multiplied by the external resistance $R = i$ under all circumstances, we have

$$e = \bar{e} - e'. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

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* The *maximal* current must not be confused with the *maximum* current. The latter would be obtained by rotating the armature in the saturated field at a very high speed in a circuit of resistance so small that the current did just not fuse the conductors. The *maximal* current is that obtained at speed n in circuit of resistance ΣR when the magnets are separately excited to saturation.

It appears, then, that in the case of the series-wound dynamo, each of the single electrical quantities is equal to the difference between the "maximal" value which that quantity could have at that speed if the field-magnet were separately saturated and the "diacritical" value of the same quantity. This important result was announced by Frölich* in 1885.

It may be remarked that, since we may write

$$H = Y\frac{E}{E+E'},$$

we may deduce from (1) the result

$$E = nB - E',$$

and from this derive equation (3).

It may be noted, in passing, that B is the electromotive forces that would be generated in the armature at speed = 1 if the field-magnets were separately excited to absolute saturation. It is the maximal value of E at unit speed.

4. *Expressions for the "Dead Turns."*

It is known that in every dynamo the current (with a given resistance) is not proportional to the speed, but is proportional to the speed less a certain number of revolutions per second. This latter number is known familiarly as the "dead turns." It is also known that (with given resistance) there is a certain speed below which the dynamo does not excite itself. This least speed of excitement (with given resistance) is the same as the "dead turns." It is called by some the "critical" speed; though that name is preferably reserved for the speed that is critical for self-regulation, and which is (unlike the least speed of excitation) independent of the resistance.

We can find an expression for the dead turns as follows:—

Taking the expression for the current,

$$i = \frac{nB}{\Sigma R} - i',$$

equate it to zero; the current of the machine (series-wound) being *nil* when n is reduced sufficiently to n' (= the dead turns); then

$$i' = \frac{n'B}{\Sigma R},$$

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[*] *Elektrotechnische Zeitschrift*, vi. p. 133, March 1885.

and

$$n' = \frac{i'\Sigma \mathrm{R}}{\mathrm{B}} \; . \; . \; . \; . \; . \; . \; . \; . \; . \qquad (5)$$

It appears, then, that the dead turns are proportional to the diacritical current and to the resistance; and inversely proportional to A and Y, the factors of B. It will be noted that $i'\Sigma\mathrm{R}=\mathrm{E}'$, the diacritical electromotive force.

Again, we have found

$$\mathrm{E} = n\mathrm{B} - \mathrm{E}' ;$$

and as $\mathrm{E}' = n'\mathrm{B}$, it follows that

$$\mathrm{E} = (n - n')\mathrm{B}. \; . \; . \; . \; . \; . \; . \; . \qquad (6)$$

This result is interesting in itself, and might have been used as a starting-point for the equations of the dynamo, inasmuch as it is readily found by experiment as a fundamental relation between speed and electromotive force. Following the analogy and the nomenclature adopted, we may regard n' (the dead turns) as the diacritical speed. In other words, it is that speed at which, with magnets separately excited to saturation, the induced electromotive force will be diacritical, and will, with the given resistances $\Sigma\mathrm{R}$, give the diacritical current. This equation (6) gives by far the best method of determining the important constant B. Two experiments to observe a pair of values of E and n will suffice to determine both n' and B.

5. *Equations of the Shunt Dynamo.*

Here we use r_s and i_s for the resistance and current of the shunt-coil, and r_a and i_a for those of the armature. We may then calculate the potential at terminals as follows. Writing $\mathfrak{R}$ for the resistance of the whole system of machine and its circuits, as measured from brush to brush*,

$$\mathrm{E} = e + r_a i_a = e\frac{r_a}{\mathfrak{R}} = 4n\mathrm{AH},$$

$$\mathrm{H} = \mathrm{Y}\frac{e}{e+e'},$$

$$e\frac{r_a}{\mathfrak{R}} = n\mathrm{B}\frac{e}{e+e'} ;$$

whence

$$e = \frac{n\mathrm{B}\mathfrak{R}}{r_a} - e'. \; . \; . \; . \; . \; . \; . \; . \; . \qquad (7)$$

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* See my 'Dynamoelectric Machinery,' second edition, p. 298.

But $\frac{nB\mathfrak{R}}{r_a}$ is the same thing as the "maximal" value of e which the machine would give, if the magnets were separately saturated, when working at the speed n through resistances as given; it may therefore be written as $\bar{e}$.

Whence, finally,

$$e = \bar{e} - e'. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

From which we get at once also for the shunt-current,

$$i_s = \bar{i} - i_s'; \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

and for the main-circuit current,

$$i = \bar{i} - i'. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

6. *General Equation of the Self-exciting Dynamo.*

Let ψ be any one of the currents or potentials of the dynamo, $\bar{\psi}$ its "maximal" value, that is to say the value it has when the magnet is separately saturated, and ψ' its "diacritical value."

$$\bar{\psi} = f(n, A, Y, [R]) ;$$

and, by the very nature of the case, whatever the form of the function f,

$$\psi = f(n, A, H, [R]) ;$$

and

$$H = Y \frac{\psi}{\psi + \psi'} ;$$

whence

$$\psi = \bar{\psi} \frac{\psi}{\psi + \psi'}$$

and, finally,

$$\psi = \bar{\psi} - \psi' ; \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

which is the general equation of the self-exciting dynamo.

It may here be pointed out that the two terms on the right-hand side of this equation—the "maximal" and "diacritical" values of the quantity on the left—possess certain properties. In a given dynamo the "diacritical" term is a constant, whilst the "maximal" term is a variable which increases with the speed of driving. The maximal term when representing a current varies also with changes of resistance, in an inverse way, but differently in shunt dynamos from series dynamos: when it represents an electromotive force it does not vary with changes of resistance. A year ago Dr. Frölich sought to divide the equation of the dynamo into two parts—an armature part and a field-magnet part. This does not quite correspond to the case. The "diacritical" term appertains to field-magnet primarily; but since the number of ampere-turns of current that will produce a half-saturated magnetic field depends also on the quantity and quality of the iron in the machine, it is impossible to regard it as independent of the iron masses of the armature. The "maximal" term is proportional both to A, the total effective area of the armature-coils, and to Y, the maximum value of the magnetic field. The "diacritical" term for currents is lowered by increase in the number of magnetizing coils, and for potentials is raised by increase in the resistance of the magnetizing coils. The "maximal" term is not altered by altering the magnetizing coils, but increases with an increase in the number of coils of the armature, and, for currents, decreases with increasing resistance. If the iron parts of a dynamo be given of a certain form, size, and quality, then it may in general be said that ψ' depends only on the windings (and, for currents, on the resistance) of the field-magnet, and $\bar{\psi}$ depends only on the windings of the armature (and, for currents, on its resistance) and not upon the windings of the field-magnet, or on their resistance except (and this only for currents) so far as their resistance contributes to the resistance of the whole circuit through which the current generated in the armature flows.

7. *Conditions of Self-regulation for Compound-wound Dynamos.*

In this case we write the formula of the electromagnet in terms of the ampere-turns; Si_a for the excitation due to the coils in the armature part of the circuit, Zi_s for that due to the shunt, and ϕ' as the diacritical number of ampere-turns. Then, writing

$$E = 4nAH;$$

$$e = E - (r_a + r_m)i_a;$$

$$YH = \frac{Zi_s + Si_a}{Zi_s + Si_a + \phi'} = Y\frac{Zi_s + Si_a}{\phi}, \text{ by equation (11) } \textit{ante};$$

$$B = 4AY;$$

we have

$$e\phi' = i_s Z(nB-e) + i_a\{S(nB)-e) - (r_a+r_m)\bar{\phi}\}. \quad . \quad (12)$$

The condition sought is to be such as to make e constant. Now ϕ' is a constant, so is i_s if e is, and n may be made constant at any value we please. Hence, as i_a is a variable, the condition of constancy can only be attained by giving the dynamo such a speed n_1 that the coefficient of i_a shall be zero, or that

$$S(n_1B-e) = (r_a+r_m)\bar{\phi}. \quad . \quad . \quad . \quad . \quad (13)$$

But $\bar{\phi}$, the maximal number of ampere-turns, is not itself a constant, since it contains as one of the three terms in its sum the quantity Si_a. Hence we gather that absolute self-regulation is physically impossible; and it approaches to perfection as $Zi_s + \phi'$ are great as compared with Si_a. In other words, there must be so much iron in the machine that the diacritical excitement is very great, and it must have a small armature-resistance; otherwise S (and Si_a) cannot be small as compared with Z (and Zi_s). This is known already to electric engineers. Assuming that the dynamo is well designed in these respects, $\bar{\phi}$ will be very nearly constant, and the equation of condition may be accepted as adequately true. This leaves equation (12) in the form

$$e\phi' = i_s Z(n_1B-e),$$

$$\frac{e\phi'}{i_s Z} = n_1B-e,$$

$$\frac{r}{Z}\phi' = n_1B-e.$$

Putting in this value of n_1B-e into equation (13), we have

$$\frac{r_s}{Z}\phi' = \frac{r_a+r_m}{S}\bar{\phi}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

Now ϕ' may be written either as Si_a' or as Zi_s', and $\bar{\phi}$ may be written either as $S\bar{i}_a$ or as $Z\bar{i}_s$. Choosing the second form in the first case and the first form in the second case, we may obtain

$$r_s i_s' = (r_a+r_m)\bar{i}_a;$$

or, finally,

$$e_s' = \bar{e}_{a+m}; \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

or, the diacritical value of the potential at terminals for the shunt-wound part of the circuit must be equal to the maximal value of the potential at terminals for the armature and series-wound part. The equation (14) also gives

$$\frac{\mathrm{Z}}{\mathrm{S}}=\frac{r_s}{r_a+r_m}\cdot\frac{\phi'}{\phi}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

which is more correct than the formula usually given hitherto for the ratio of the shunt- and series-windings, and which assumes absence of saturation terms.

The simplicity of these results, no less than that of the processes by which they are derived, lends additional value to the new formula of Dr. Frölich, whose work deserves to be more widely known and recognized than it now is.

City and Guilds of London Technical College,
Finsbury, June 1886.

XV. *The Expansion of Mercury between* 0° C. *and* −39° C. *By* Professors W. E. Ayrton, *F.R.S.*, *and* John Perry, *F.R.S.*[*]

At a meeting of the Physical Society in November 1885, Mr. G. Whipple gave the Society the results of the examination of thermometers down to the melting-point of mercury. There was, however, no evidence as to whether the contraction of the mercury was uniform, as the thermometers were only compared with mercurial ones, and as, in addition, we were not able to find the results of any experiments made on the expansion of mercury between 0° and −39° C., its temperature of solidification, we thought it desirable to make a series of comparisons of a mercury-thermometer, the stem of which had been accurately subdivided into equal volumes, with an air-thermometer, both immersed in a bath of frozen mercury which was allowed to gradually become warm. For this purpose we borrowed a mercury-thermometer from Mr. Whipple, which he was so kind as to lend us, and one of our assistants (Mr. Mather) constructed a very simple form of constant-volume air-thermometer, shown in the diagram.

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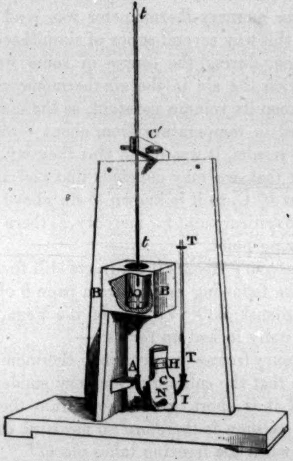
[*] Read March 27, 1886.

B B is a wooden box, at the bottom of which is a hole closed by an india-rubber stopper through which passes tightly the glass stem of an air-thermometer, A A. The bottom of the air-thermometer is attached by a piece of india-rubber tubing, I I, to a vertical glass tube, T T; and the thermometer being filled with dry air, some mercury is introduced into the tube so as to stand at about the same height in the two limbs when the air in the bulb *b* is at atmospheric pressure. The height of the level of the mercury can be varied by turning the nut, N, which causes the clamp, C, turning on the hinge H, to squeeze the india-rubber tube more or less tightly, and so to alter its internal capacity; and in this way the level of the mercury in the left-hand tube can be kept quite fixed, and therefore the volume of air in the bulb *b* quite constant, while its temperature is altered, the corresponding pressure being of course measured by the difference between the levels of the mercury columns in the two limbs.



To perform the experiment, the box B B was first filled with mercury and frozen by stirring carbonic-acid snow and ether up with it; and when sufficient of the mercury was frozen, the bulb of the mercurial thermometer, *t t*, was introduced into the pasty mercury, and the thermometer fixed in position by means of the clamp, C′. The nut N was now turned by one observer until the level of the mercury in the left-hand limb came opposite a *fixed* mark on the tube which is only just below the bottom of the box, when the height of the mercury in the right-hand tube was read by a cathetometer made by the Cambridge Instrument Company, and the position of the mercury in the mercury-thermometer was read by a third observer. In this way several series of simultaneous observations were taken, during the course of some weeks, of the pressure to which the air in the air-thermometer had to be subjected to keep its volume constant, as the mercury in the box B B varied in temperature from about $-39°$ C. to $0°$ C. Plotting these results, it was found that they lay in so nearly a straight line that we may conclude that mercury expands regularly below $0°$ C. as it is known to do above $0°$ C.; and that there is no critical point for mercury, as there is for water, above the freezing-point.

When the mercury freezes it contracts still further, as may be seen from the following extract from page 6 of the second volume of Nordenskiöld's 'Voyage of the Vega,' which Mr. Whipple has kindly looked up for us:—

"When mercury freezes in a common thermometer, it contracts so much that the column of mercury suddenly sinks in the tube, or, if it is short, goes wholly into the ball. The position of the column is therefore no measure of the actual degree of cold when the freezing takes place."

We have to express our thanks to Messrs. Chatterton, Humphrey, and Martin, three of the students of the Central Institution, for assistance rendered in the carrying out of this experiment.

XVI. *On the Expansion produced by Amalgamation. By* Professors W. E. Ayrton, *F.R.S., and* John Perry, *F.R.S.*[*]

On amalgamating the edge of a brass bar, nearly three quarters of an inch thick and about a foot long, for the purpose of enabling the edge to make good electric contact with a plate, we were surprised to find that the bar rapidly curved, the amalgamated edge becoming convex, exactly as happens when one side of a piece of paper is wetted. On hammering the bar to straighten it, the curvature became instead greater. Seeing that to bend a short brass bar more than half an inch in thickness to the extent produced by the amalgamation of the edge requires the exertion of very considerable stresses, it follows that very great forces must be produced by amalgamation.

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[*] Read March 27, 1886.

We think it possible that this bending by amalgamation may be an important cause in the production of the Japanese "magic mirrors," the reflecting surface of which is polished with a mercury amalgam. Japanese mirrors are made of bronze and have a raised pattern cast on their backs; and although the eye can detect no trace of the pattern on looking at the polished reflecting surface, yet when certain of these mirrors are used to reflect a divergent beam on to a screen, the pattern at the back can be seen as a bright image on a dark ground. In a paper communicated, some years ago, to the Royal Society, we showed that this peculiar effect arose from the fact that, while the reflecting surface was generally convex, the portions corresponding with the pattern or thicker parts were less convex (that is, more concave) than the rest; and this conclusion we verified by finding that when a convergent, instead of a divergent, beam of light was allowed to fall on the mirror the image on the screen was reversed; that is, the pattern was seen as a dark image on a bright ground.

This inequality of curvature we considered at that time was due partly to the pressure of the "distorting-rod" used to make the surface convex, and partly to the pressure exercised on the subsequent polishing; but we now think that, in addition, the action of the mercury-amalgam employed by the polisher may assist in making the thin portions of the mirror more concave than the thicker.

XVII. *On certain Sources of Error in Connection with Experiments on Torsional Vibrations.* *By* HERBERT TOMLINSON *B.A.*[*]

Introduction.

DURING a long series of researches on the torsional elasticity and internal friction of metals, I have come across certain sources of error in connection with torsional vibrations generally, which I venture to bring before the notice of the Physical Society in the hope that by so doing I may perchance save others who may pursue similar investigations from the pitfalls into which I have fallen, and from which I have managed to extricate myself only after a considerable expenditure of time and labour.

In my earlier experiments a wire about 600 centims. in length and 1 millim. in diameter was suspended vertically, having its upper extremity clamped to a rigid support and its lower one clamped or soldered to the centre of a horizontal bar of brass, from which were suspended, by *threads or fine wires*, two cylinders of equal dimensions and mass, and placed at equal distances from the wire. The torsional oscillations of the wire were observed by means of the usual arrangement of mirror, scale, and lamp, the main object of the inquiry being to determine as accurately as possible the logarithmic decrement of the amplitude of swing and the vibration-period. After one set of observations had been completed, the moment of inertia was altered by sliding the cylinders along the bar further away from or nearer to the wire, so that the latter might now vibrate in a different period. If t be the period of vibration, k the moment of inertia, and f the torsional couple,

$$f=\frac{\pi^2 k}{t^2}.$$

The moment of inertia of the bar together with that of the suspended cylinders could be calculated with very fair accuracy; the value of t was also calculated to a nicety; so that it was reasonable to expect that the values of f obtained with different moments of inertia should be very fairly in accordance with each other. For some time this proved to be the case, and several wires of different metals had already been examined when a curious phenomenon presented itself. A change of moment of inertia had just been made, and the wire was then set in torsional oscillation; but instead of the amplitude of swing diminishing by slow degrees as in the previous experiments, the spot of light was seen to make five or six oscillations of very rapidly diminishing amplitude, and finally come nearly to rest. Soon, however, the amplitude began to increase until in a few vibrations it extended over some two hundred divisions of the scale, when once more diminution and, finally, rest nearly ensued. I will not trouble the Society with my conjectures at the time as to the cause of the phenomenon; suffice it that at length I discovered, what perhaps I ought to have discovered at once, that the, at first sight, startling apparition was due to a very natural cause, namely, the rotation to and fro of the cylinders about their axes, and that the rapid absorption of energy was owing to the fact that the torsional vibration-period of the wire nearly synchronized with the vibration-period of the cylinders about their axes. I need hardly say that after this discovery I considered it necessary to re-try all my previous experiments with improved arrangements. With more perfect apparatus, in which the cylinders were clamped to the bar so as to be incapable of motion independently of the latter, I was glad to find the main conclusions which I had previously drawn respecting internal friction confirmed. On one occasion, however, by what afterwards turned out to be the merest chance in the world, the old phenomenon appeared with all its curious concomitants, and beats were very plainly discernible between two sets of vibrations which nearly synchronized. These two sets of vibrations I set to work to disentangle in a manner kindly suggested to me by Prof. G. G. Stokes, with whom I had some correspondence on the subject. Suppose that in one or more beat-intervals the slower vibration is dominant*, and afterwards the quicker. If the amplitudes cross during a beat-interval, that one is to be deemed dominant which is dominant about the time of lull. Suppose there are *m* beat-intervals in which the slower is dominant, followed by n in which the quicker is dominant, and let N be the total number of vibrations counted[*]. Then the number of vibrations of the two component kinds will be:—

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[*] Read June 26, 1886.

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* By dominant vibration is meant the vibration of greater amplitude.

$$\text{For the slower, } N-2n,$$
$$\text{For the quicker, } N+2m.$$

In this way I managed without any difficulty to find that one of the two vibration-periods was nearly a constant whatever the moment of inertia; whilst the other, that due to the torsional elasticity of the wire, increased as the square root of the moment of inertia. At first I felt very strongly inclined to believe that the former of the two vibration-periods pertained to some molecular state of the wire; and I was especially deceived by the fact that always after rest the phenomenon became less marked, and, finally, almost vanished, easily, however, to be reproduced in all its former intensity by the slightest shock given to the wire, or by raising or lowering the temperature slightly. The wire was of iron, and my previous experience of the effect of rest on the molecular disposition of this metal led me to draw the above-mentioned conclusion. Had I not been thus deceived, I might more quickly have arrived at the solution of the problem; but as it was four weeks were spent in endeavouring to find the effect of change of temperature, change of load, and change of mode of attaching the cylinders, until I discovered that the phenomenon was simply caused by approach to synchronism between the periods of torsional and *pendulous* vibrations of the wire. Of course, if the axis of the wire passed accurately through the centre of mass of the vibrator, the phenomenon would not occur, but it is impossible *quite* to secure this; and as a consequence so-called centrifugal force on the one hand, and the force of gravity on the other, set up pendulous vibrations which may seriously interfere with the vibration-period due to the torsional elasticity, and still more so with the logarithmic decrement of arc.

Having thus discovered two enemies in ambush, I thought that the ground was now clear, at least as far as any danger from synchronism was concerned; but in this I was mistaken: for happening to pursue my investigations still further with comparatively light loads and small moments of inertia, I at length became acquainted with a third source of error arising from approach to synchronism between the torsional and *transverse* vibrations of the wire. It is, I believe, quite impossible to excite torsional vibrations without at the same time exciting transverse ones; and should synchronism nearly occur between the periods of these vibrations, we may have beats quite as strongly marked as in the two cases before mentioned.

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[*] For accuracy, the counting should begin and end with a maximum.

There is yet another source of error to which it is desirable to draw attention. When a wire has been recently suspended, the torsional vibration-period will always be found slightly greater than when it has been suspended for some time and frequently set in vibration. The length of time which must elapse before a wire has reached its state of maximum torsional elasticity depends upon the nature of the metal; with copper, for instance, a few hours will suffice, whilst iron may require at least a couple of days. Now suppose that this state of maximum elasticity has been reached: if we wish to preserve it, care must be taken not to jar the wire or to subject it to a change of temperature of even two or three degrees Centigrade; for in either case the elasticity will be slightly diminished, and a few hundred vibrations will be required to restore it to its former condition. Since it is very difficult to avoid such slight changes of temperature as those mentioned above, it is always advisable after any rest to cause the wire to vibrate a few hundred times before beginning fresh observations.

Determinations of Torsional Electricity.

It is evident, from what has gone before, that when the cylinders are suspended from the bar by threads, the torsional elasticity, *as inferred from the vibration-period*, may be seriously affected should the torsional vibration-period of the wire approach to synchronism with the vibration-period of the cylinders about their axes; and to such an extent did I find this to be the case, that the values of the torsional couple for the same wire, as calculated from the previously given formula, differed from each other by 10 per cent. or more when the moment of inertia was varied.

The effect of synchronism between the torsional vibrations of the wire and the pendulous vibrations is not likely, if proper care be taken in the construction and disposition of the bar and its appendages, to be great; but it may nevertheless be very sensible.

Synchronism between the torsional and transverse vibration-periods is not likely to occur except in extreme cases; but it must be remembered that the torsional vibration-periods may be affected by synchronism between them and *multiples* of the transverse vibration-period, though of course not to the same extent as when the fundamental transverse vibration-period equals the torsional vibration-period. A similar remark to the above would also apply to the other two cases of synchronism.

Determinations of Magnetic Moments.

It is evident that determinations of magnetic moments by the method of oscillations may be similarly affected by the same causes as we have seen would affect determinations of the torsional elasticity.

Damping of Magnets.

Still greater error may be introduced from the above causes in experiments on the damping of vibrating magnets; for the logarithmic decrement is much more seriously affected than the vibration-period.

Determinations of Moments of Inertia.

When it is impossible to determine the moment of inertia of a body by measurement of its dimensions and mass, it is usual to find the time of oscillation, and afterwards to redetermine this time when the moment of inertia has been altered to a known extent.

If t and t' be the two times of oscillation, K the required moment of inertia, and k the known change of moment of inertia,

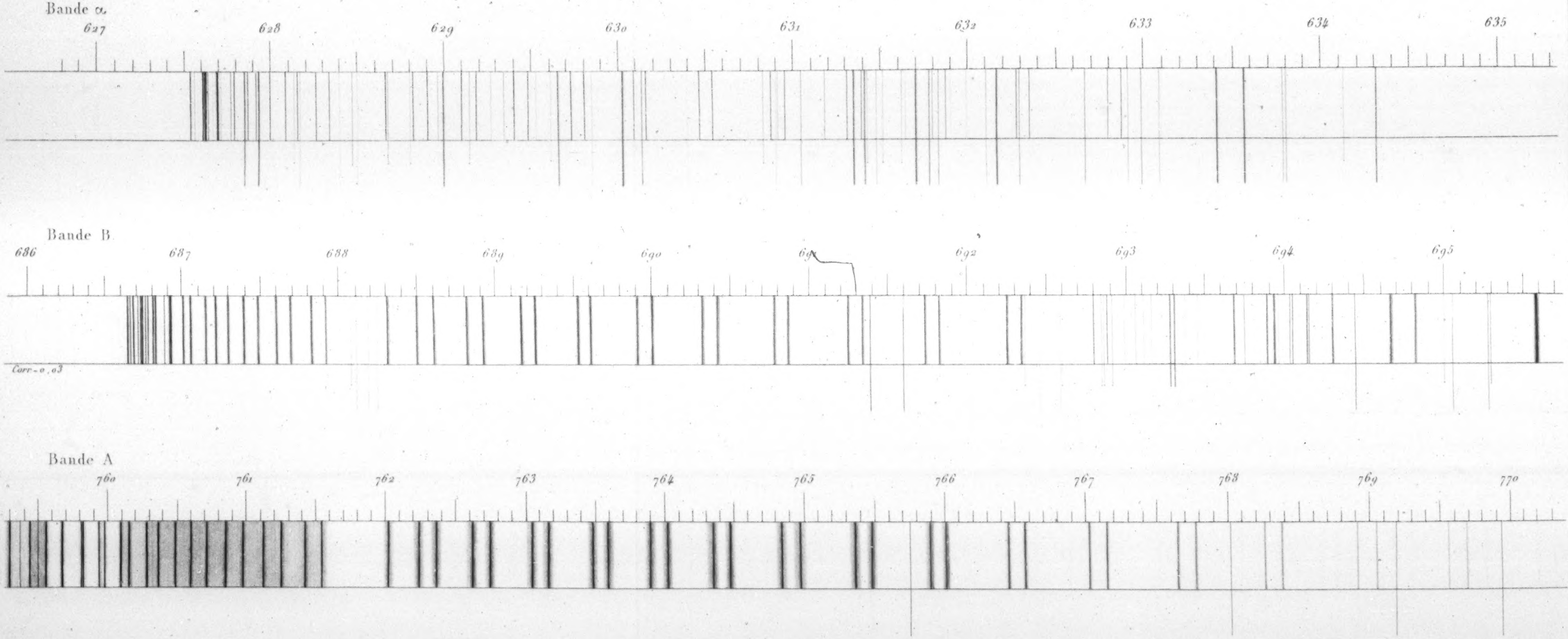
$$K = k\frac{t^2}{t'^2 - t^2}.$$

Annales de Chimie et de Physique. 6e Série. Tome VII. (Janvier 1886.)

Proc. Phys. Soc. vol. 8, Pl. II.

Étude des bandes telluriques α, B et A du spectre solaire,

par M. A. Cornu



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Now a small error in the determination of either t or t' produces a comparatively large error in the value of K; and it is therefore of considerable importance here that there should be no approach to the previously mentioned synchronisms. It is important also here to notice the fourth source of error which has been mentioned; for it is very difficult to change the moment of inertia without imparting some shock to the wire.

XVIII. *On the Distinction between Spectral Lines of Solar and Terrestrial Origin. By* Prof. M. A. CORNU[*].

[Plate II.]

FRAUNHOFER, when he discovered the dark lines with which the solar spectrum is crossed, gave them names in order to facilitate description; the principal lines were designated by the letters A, B, . . . H in such a way as to separate approximately the seven principal colours of the spectrum. The subsequent observations of Brewster, Dr. Gladstone, and M. Janssen proved that, notwithstanding the symmetry of denomination and the identity of appearance, these dark lines belonged to two distinct classes. Indeed, the one preserves always the same aspect, while the other becomes broader and darker as the sun approaches the horizon.

The first, most of which have been identified with the bright lines due to metallic vapours (iron, magnesium, calcium, nickel, &c.), have been attributed, since the researches of Prof. Kirchhoff, to the absorption produced by metallic substances in a state of vapour on the surface of the sun. The other, in consequence of their intensity varying with the thickness of the atmosphere traversed by the sun's rays, are explained by the selective absorption due to the cold gases or vapours of the earth's atmosphere. We ought then to distinguish the *solar* from the *telluric* lines.

Thus, of the eight principal Fraunhofer-lines, six are characteristic of metallic elements and are of solar origin (C and F, hydrogen; D, sodium; E, G, iron; H, calcium); the other two (A and B) are telluric.

Fraunhofer had besides distinguished two complex groups, namely a band a, very broad, in the extreme red, and a well-marked triple line, *b*, in the green; *b* is solar (magnesium), and *a* of terrestrial origin (fig. 1). Brewster, on discovering new bands of variable intensity in the spectrum, added new designations; it is sufficient here to mention the band *α* situated in the orange, and the band *δ* in the yellow. These symbols have been adopted by Ångström (*Spectre normal du Soleil*).

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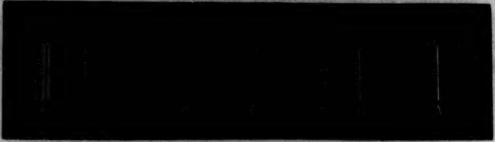
[*] Read June 12, 1886.

Fig. 1.



Solar spectrum, with principal lines marked.

Up to the present time it has been considered a difficult, and in any case a troublesome, matter to distinguish between these two kinds of lines. It was necessary, in fact, to observe the solar spectrum at two very different altitudes of the sun, under various meteorological conditions, to be able to affirm that the spectrum-lines do or do not change in intensity with the thickness of the atmosphere or the quantity of water-vapour traversed by the solar rays.

The improvement of spectroscopes, in respect of the sharpness and especially of the dispersion of the lines, has allowed me to arrive at a method which renders the distinction between the two kinds of rays in a certain sense *intuitive*.

This method is founded on a principle due to M. Fizeau*—the principle of the displacement of the spectral lines of the light emitted by a source which is in absolute or relative motion. We easily obtain the expression for the apparent wave-length λ' of a radiation from a point in motion with a relative velocity v, the true wave-length being λ, viz.:—

$$\lambda' = \lambda\left(1 - \frac{v}{V}\right).$$

This principle may be applied directly to the light emitted by the solar disk at the two extremities of an equatorial diameter.

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* *Bulletin de la Société Philomathique*, décembre 1848; and *Ann. de Chim. et de Phys.* 4 série, t. xix. p. 211.

The absolute velocity v of a point on the solar equator is very sensibly 2 kilometres per second, that of the velocity of light, V, 300,000 kilometres per second. Hence we shall have a variation of wave-length equal to

$$\Delta\lambda = \pm\lambda \times \frac{2}{300{,}000} = \pm\frac{\lambda}{150{,}000},$$

+ or − according as we take the same radiation at the eastern or western end of the solar equator.

If we wish to know numerically the magnitude of the displacement of a spectral line corresponding to this variation of wave-length, it is sufficient to substitute for λ the numerical value which defines the region which we wish to observe. Consider, for example, the two D lines ($\lambda_1 = 588{\cdot}40, \lambda_2 = 588{\cdot}89$). The displacement of a line having $\lambda = 589$ will be

$$\Delta\lambda = \pm\frac{589}{150{,}000}.$$

If we wish to compare this displacement with the distance between the two D lines (*i. e.* with $\lambda_2 - \lambda_1 = 0{\cdot}49$), we shall have as the relative displacement,

$$\frac{\Delta\lambda}{\lambda_2 - \lambda_1} = \pm\frac{589}{{\cdot}49 \times 150{,}000} = \frac{1}{124{\cdot}8}.$$

The double displacement will therefore be $\frac{2}{124{\cdot}8}$ or $\frac{1}{62{\cdot}4}$ of the distance between the two D lines.

This total displacement, small as it is, is perfectly appreciable with spectroscopes of very high dispersion, such as the prism-spectroscope of M. Thollon, and the instruments with diffraction-gratings constructed by Prof. Rowland of the University of Baltimore.

With the magnificent grating presented by Prof. Rowland to the École Polytechnique, the double displacement may become sensible almost with all the points of the solar contour; that is to say, even with those which are far from giving the maximum separation.

The experimental method consists in causing the images of the two extremities of the solar equator to fall alternately on the slit of the spectroscope. For this purpose the solar beam is received on a condensing-lens, which produces in the plane of the slit a sharp image of the solar disk. The substitution of one of the extremities for the other produces the double displacement of the solar radiations, while it has no influence upon the position of the absorption-lines of the atmosphere.

The analysis of the optical conditions shows that perfect sharpness of the displacement can only be obtained when three experimental conditions are fulfilled :—

1. The spectral images at the focus of the telescope of the spectroscope must be *aplanatic* ; that is, such that the vertical lines (spectral lines) and the horizontal lines (due to the imperfections of the slit) are equally sharp in the same plane.

2. This plane must coincide accurately with that of the cross wires.

3. The focal image of the solar disk must be exactly in the plane of the slit of the collimator.

The omission of any one of these adjustments would involve an abnormal displacement of the lines consequent upon a displacement of the collecting-lens. On the other hand, when all these adjustments have been made the dark lines of terrestrial origin are perfectly fixed, while those of solar origin move with extreme sharpness.

If we take as a fixed mark a dust particle on one of the cross wires, such as are always to be found on wires, we are able to distinguish immediately, *at a glance*, solar from telluric rays.

Finally, I may add that the displacement becomes still more sensible when the substitution of one solar edge for the other is effected rhythmically. This is done by causing the collecting-lens to oscillate two or three times per second [*].

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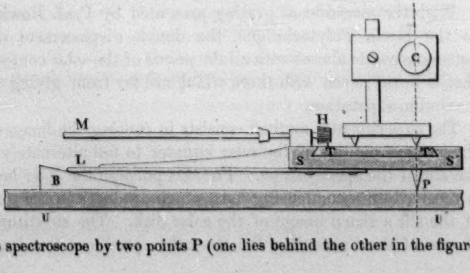
[*] The following (see fig. 2) is the arrangement employed:—The collecting-lens C is carried by a socket S S′ which rests on the table U U′ of the spectroscope by two points P (one lies behind the other in the figure),

Fig. 2.



The eye then becomes sensitive to the least oscillation of the lines.

The distinguishing of the lines becomes then entirely intuitive. We observe each spectral line, and the result is such as would be produced by shaking it. If it remains immovable, it is a telluric line; if it oscillates, it is a solar line.

The study of the telluric lines of the solar spectrum becomes therefore infinitely easier than heretofore. I have devoted to this study the fine days of the last few years, and the results have been very fruitful. Amongst the most interesting of the observations I may mention :—(1) the *anatomy* of Ångström's group α (see Plate II.), in which I have succeeded in detecting a group possessing the same constitution as the bands A and B, according to the beautiful observation of Prof. Langley; (2) the telluric nature of a certain number of lines beyond the band δ; and (3) the solar origin of the line 1474 of Kirchhoff: this line is double under strong dispersion, and as it oscillates we may conclude that the vapour which absorbs the radiations of which it takes the place is carried round by the rotation of the sun[*].

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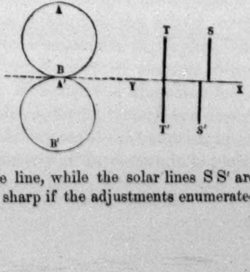
about which it can turn. The optic centre C of the collecting-lens describes a small horizontal element, and transmits the same motion to the image of the solar disk. The observer produces this motion by the aid of the lever L. The pinion H serves to put the collecting-lens exactly in focus on the slit.

[*] The oscillation of the lines is not the only means of distinguishing the two kinds of lines. If (by means of a Wollaston's double refracting-prism) we obtain two images of the solar disk in such a way that the two opposite extremities of the equatorial diameter are tangent and normal to the slit (fig. 3), the telluric lines T T′ of the spectra of the two images are upon the same line, while the solar lines S S′ are dislocated. This dislocation is very sharp if the adjustments enumerated above have been

Fig. 3.



To sum up:—Physicists and astronomers have now in their hands an extremely useful method for studying the constitution of the solar spectrum, a method which enables us to distinguish at a glance between lines of solar and terrestrial origin.

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properly carried out; otherwise we obtain the confused appearance of fig. 4. If we employ a collecting-lens of very short focus, giving a very small image of the solar disk, it is easy to show that the appearance of the figure (3) is modified. The telluric lines remain vertical, while the solar lines are not only dislocated, but become oblique (see fig. 5). We have here a very delicate test which lends itself to photographic observations.

Fig. 4.

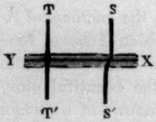
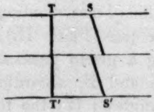


Fig. 5.



PROCEEDINGS

OF

THE PHYSICAL SOCIETY

OF LONDON.

JANUARY 1887.

XIX. *The peculiar Sunrise-Shadows of Adam's Peak in Ceylon.*

By the HON. RALPH ABERCROMBY, *F.R. Met. Soc.*[*]

THERE are certain peculiarities about the shadows of Adam's Peak which have long attracted the attention of travellers: a good deal has been written about them, and several theories have been proposed to explain the observed phenomena. In the course of a meteorological tour round the world, the author stopped in Ceylon for the express purpose of visiting the Peak, and was fortunate enough to see the shadow under circumstances which could leave no doubt as to the true explanation, and which also entirely disproved certain theories which have been propounded on the subject.

The following account is taken from a paper by the Rev. R. Abbay, many years resident in the island, entitled "Remarkable Atmospheric Phenomena in Ceylon," which was read before the Physical Society of London, May 27, 1876, and published in the Philosophical Magazine for July 1876. Writing from descriptions, for he himself had never witnessed the appearance, Mr. Abbay says:—At sunrise apparently an enormous elongated shadow of the mountain is projected to the westward, not only over the land but over the sea, to a distance of 70 or 80 miles. As the sun rises higher, the shadow rapidly approaches the mountain, and appears at the same time to rise before the spectator in the form of a gigantic pyramid. Distant objects—a hill or a river (or even Colombo itself, at a distance of 45 miles)—may be distinctly seen through it; so that the shadow is not really a shadow on the land, but a veil of darkness suspended between the observer and the low country. All this time it is rapidly rising and approaching, and each instant becoming more distinct, until suddenly it seems to fall back on the spectator, like a ladder that has been reared beyond the vertical; and the next instant the appearance is gone. For this the following explanation is proposed :—The average temperature at night in the low country during the dry season is between 70° and 80° F., whilst that on the summit of the Peak is from 30° to 40°. Consequently the lower strata of air are much less dense than the upper; and an almost horizontal ray of light passing over the summit must of necessity be refracted upwards and suffer total internal reflection as in the case of an ordinary mirage.

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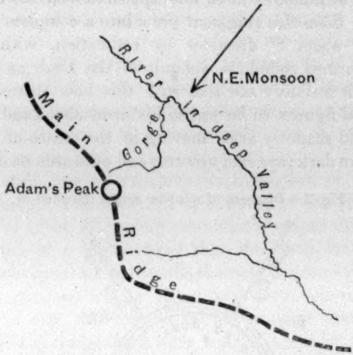
[*] Read November 13, 1886.

It will be remarked that Mr. Abbay does not allow for the difference of elevation, and the sequel will show that this theory cannot be maintained.

Adam's Peak is a mountain that rises in an abrupt cone, more than 1000 feet above the irregular chain to which it belongs; the summit reaches to 7352 feet above the sea. On the south side the mountain falls suddenly down to Ratnapura, very little above the sea-level; while on the north it slopes irregularly to the high valley of the Maskeliya district. The peak also lies near an elbow in the main chain of mountains, as shown in the diagram of the topography of the Peak (fig. 1), while a gorge runs up from the north-east just to the west of the mountain. When, then, the north-east monsoon blows morning mist up the valley, light wreaths of condensed vapour will pass to the west of the Peak and catch the shadow at sunrise only, if other things are suitable. The importance of this will appear later on.

The only difficulty in getting to Adam's Peak is the want of a rest-house within reasonable distance of the summit. Fortunately the kindness and hospitality of T. N. Christie, Esq., of St. Andrew's Plantation, Maskeliya, enabled the author, in company with Mr. G. Christie and Professor Bower, of the University of Glasgow, to make the ascent with great comfort and with a few necessary instruments. Our party reached the summit on the night of the 21st February, 1886, amid rain, mist, and wind. Towards morning the latter subsided, but at 5.30 A.M the sky was covered with a confused mass of nearly every variety of cloud. Below and around us cumulus and mist ; at a higher level, pure stratus ; above that, wild cirro-stratus and fleecy cirro-cumulus.

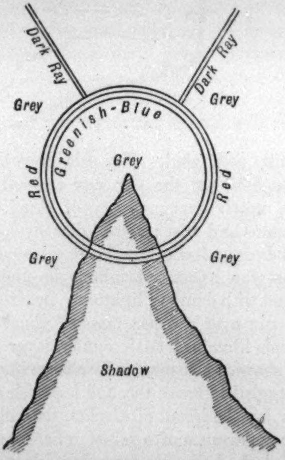
Fig. 1.—Diagram of the Topography of Adam's Peak.



Soon the foreglow began to brighten the under surface of the stratus-cloud with orange ; lightning flickered to the right of the rising sun over a dense mass of cloud ; opposite, a light pink-purple illumined an irregular layer of condensed vapour ; while above, a pale moon with a large ill-defined *corona* round her struggled to break through a softish mass of fleecy cloud. Below lay the island of Ceylon, the hills and valleys presenting the appearance of a raised relief-map ; patches of white mist filled the hollows ; true cloud drove at intervals across the country, and sometimes masses of mist coming up from the valley enveloped us with condensed vapour.

At 6 A.M. the thermometer marked 52° F. ; we had been told that the phenomenon of the shadow depended on the temperature at the summit falling to 30° or 40° F.; and when, shortly after, the sun rose behind a cloud we had almost lost all hope of seeing anything; but suddenly at 6.30 A.M. the sun peeped through a chink in the clouds, and we saw the pointed shadow of the Peak lying on the misty land. Driving condensed vapour was floating about, and a fragment of rainbow-tinted mist appeared near the top of the shadow. Soon this fragment grew into a complete prismatic circle of about 8° diameter by estimation, with the red outside, formed round the summit of the Peak as a centre. The author instantly saw that with this bow there ought to be spectral figures, so he waved his arms about and immediately found shadowy arms moving in the centre of the rainbow. Two dark rays shot upwards and outwards on either side of the centre, as shown in the diagram fig. 2, and appeared to be nearly in a prolongation of the lines of the slope of the Peak below. The centre of the bow appeared to be just below the point of the shadow, not on it; because we were

Fig. 2.—Diagram of rainbow round the shadow.



standing on a platform below a pointed shrine, and the subjective bow centred from our own eyes. If we did not stand fairly out in the sun, only a portion of the bow could be seen. Three times, within a quarter of an hour, this appearance was repeated as mist drove up in proper quantities, and fitful glimpses of the sun gave sufficient light to throw a shadow and form a bow. In every case the shadow and bow were seen in front of land and never against the sky. The last time, when the sun was pretty high, we saw the characteristic peculiarity of the shadow. As a thin wreath of condensed vapour came up from the valley at a proper height, a bow formed round the shadow, while both seemed to stand up in front of us, and then the shadow fell down on to the land, and the bow vanished as the mist passed on.

Here, then, was an unequivocal explanation of the whole phenomenon. The apparent upstanding of the shadow was simply the effect of passing mist which caught the darkness of the Peak at a higher level than the earth, for when the condensed vapour moved on, the characteristic bow disappeared and the shadow fell to its natural plane on the ground. When the mist was low, as on the two first occasions, the shadow fell on the top as it were, and there was no appearance of lifting, only the formation of a bow.

The well-known theory of the bow is that light diffracted in its passage between small water-globules forms a series of bows according to the size of the globules, their closeness, and the intensity of the illumination. Had the mist been so fine and thin as merely to catch and raise the shadow, but not to form a bow, there might have been some doubt as to the origin of the appearance. Our fortune was in the unsettled weather, which made the mist so coarse and close that the unequivocal bow left no doubt as the true nature of the cause.

About an hour later the sun again shone out, but much higher and stronger than before, and then we saw a brighter and sharper shadow of the Peak, this time encircled by a double bow. Our own spectral arms were again visible, but the shadow was now so much nearer the base of the Peak, and we had to look so much down on it, that there was no illusion of standing up, and there were no dark diverging rays. The inner bow was the one we had seen before; the outer and fainter one was due to stronger light.

The bows were all so feeble and the time so short, that the author did not succeed in obtaining any sextant measurements of the diameters of the bows; but his thermometric observations conclusively disprove any idea of mirage. At 6 A.M. the thermometer on the Peak marked 52° F., while at Colombo the temperature stood at 74°·85. The difference of 22°·85 is just about the normal difference in temperature due to a height of 7352 feet.

The Colombo figures were procured through the courtesy of the Surveyor-General for Ceylon. They are got as follows:—Colombo observations only give the *minimum* that morning as 73°·6 F., and the 7 A.M. reading as 75°·5. The mean curve of diurnal temperature for the month of February, as determined by the Office, gives a difference of 0°·65 between the 6 A.M. and 7 A.M. observations; and by subtracting that correction from 75°·5 we get 74°·85 as the 6 A.M. reading.

The questions have been frequently asked—Why this lifted shadow should be peculiar to Adam's Peak?; why a similar appearance is not observed from any other mountain-top?; and why the shadow is rarely seen at sunset? There are not many mountains which are habitually visited that are either over 7000 feet, or that rise in an isolated, well-defined pyramid. Still fewer can there be where a steady wind, for months together, blows up a valley so as to project the rising morning mist at a suitable height and distance on the western side to catch the shadow of the peak at sunrise. The shadow is not seen during the south-west monsoon, for then the mountain is covered with cloud and deserted. Nowhere either do we find at sunset those light mists lying near the ground which are so characteristic of sunrise, and whose presence is necessary to lift the shadow.

The combination of a high isolated pyramid, a prevailing wind, and a valley to direct suitable mist at a proper height on the western side of the mountain, is probably only rarely met with; and at present nothing yet has been described that exactly resembles this sunrise shadow of Adam's Peak in the green island of Ceylon.

But there is another totally different shadow which is sometimes seen from Adam's Peak, just before and at the moment of sunrise, that has been mixed up in some accounts with the shadow we have just described. The shadow of the base of the Peak stretches along the land to the horizon, and then the shadow of the summit appears to rise up and stand against the distant sky. The first part seems to be the natural shadow lying on the ground ; and the sky part to be simply the ordinary earth shadow of twilight projected so clearly against the sky as to show mountainous irregularities of the earth's surface. As the sun rises, the shadow of the summit against the sky gradually sinks to the horizon, and then the ordinary shadow grows steadily shorter as the sun gets higher in the usual manner. This can only be seen at sunrise from Adam's Peak, because the ground to the east is too high and mountainous to allow the shadow of the summit to fall on the sky before the sun is too far down.

The author found a similar effect, only at sunset, on Pike's Peak, Colorado, 14,147 feet above the sea, and nearly double the height of Adam's Peak. There, towards sunset, the shadow of the mountain creeps along the level prairie to the horizon, and there begins to rise up in the sky till the sun has just gone down, and the anticrepuscular shadow rises too high to catch the outline of the Peak. The author only witnessed a portion of this sequence, for just about the time that the shadow stretched to the horizon, clouds obscured the sun, and the rise of the shadow could not be observed ; but from all the descriptions he heard, there can be no doubt that the character of the shadow is identical with that of Adam's Peak, only that, as the order of sequence is reversed, it is more easy to follow the origin of the shadows.

Since the above was written, the author's attention has been called to the sketch of the shadow exhibited by the well-known traveller Miss C. F. Gordon Cumming, in the Colonial Exhibition. This picture represents the shadow lying down, but not raised, on an irregular surface of white mist and mountain tops. The most interesting thing is a prismatic fringe of colour along the straight outside edges of the shadow ; but there is no trace of a bow round its point.

When we consider how much the appearance of the shadow depends on the height, size, and aggregation of the mist, we need not be surprised at the numerous phases of reflection and refraction that have been described by travellers; but the general principles which have been laid down in this paper appear to govern all.

XXI. *On the Critical Mean Curvature of Liquid Surfaces of Revolution.* *By* A. W. Rücker, *M.A., F.R.S.*[*]

Let a weightless mass of liquid, or a liquid film, be attached to two equal circular rings, the planes of which are perpendicular to the line joining their centres. It will form a surface of revolution; and if it is in stable equilibrium, the longest or the shortest diameter will be half way between the rings. It is convenient to call this the *principal diameter*. At all points on the surface the sum of the reciprocals of the two principal radii of curvature is constant. Half this quantity may be called the *mean curvature*. Maxwell has, in his article on Capillary Action (*Enc. Brit.*, 9th edition), given a simple proof of the fact that if the film is a cylinder, a slight bulge will cause an increase or decrease in the mean curvature according as the distance between the rings is less or greater than half the circumference of either. If the distance between the rings is exactly half the circumference, an infinitely small change in the volume will modify the form of the surface, but will not alter the mean curvature. Thus the mean curvature of a cylinder, the length of which has this particular ratio ($\pi/2$) to its diameter, is evidently a maximum or minimum with respect to that of other surfaces of constant mean curvature, which pass through the same rings at the same distance apart, and which differ but little from the cylindrical form. Hence the cylinder may be said to have a *critical mean curvature* when the distance between the rings is half their circumference. If the distance between the rings is altered, a similar property will be possessed by some other surface. It is proposed in the present paper to determine the general relation between the magnitude and distance of the rings and the form of the surfaces of critical curvature.

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[*] Read November 27, 1886.

The expression for the change in the mean curvature of a film or liquid mass, under the conditions above laid down, has been investigated in a paper "On the Relation between the Thickness and the Surface-tension of Liquid Films," lately communicated by Prof. Reinold and myself to the Royal Society. It was, however, applied only to the cases which were practically realized in the experiments therein described. It will be convenient, before discussing it more fully, to indicate the manner in which the equation is obtained.

Beer has shown that if the axis of x be the axis of revolution, the equation to a liquid surface of revolution is given by the expressions

$$x=\alpha E+\beta F, \quad y^2=\alpha^2\cos^2\phi+\beta^2\sin^2\phi\,; \quad . \quad . \quad (1)$$

where F and E are elliptic integrals of the first and second kinds respectively, of which the amplitude is ϕ, and the modulus $\kappa=\sqrt{\alpha^2-\beta^2}/\alpha$.

As usual

$$\Delta=\sqrt{1-\kappa^2\sin^2\phi}, \quad . \quad . \quad . \quad . \quad . \quad (2)$$

whence $y=\alpha\Delta$; and if $\kappa=\sin\theta$, $\beta=\alpha\cos\theta$.

Since $\alpha>\beta$, α and β are the maximum and minimum values of y respectively : and the above equations implicitly assume that the origin lies on a maximum ordinate; for when $\phi=0$, $x=0$ and $y=\alpha$. If we wish to transform to a minimum ordinate, ϕ is $>\pi/2$, and

$$x=\alpha(E-E_1)+\beta(F-F_1), \quad . \quad . \quad . \quad . \quad (1a)$$

where E_1 and F_1 are the complete integrals.

It may be well, for the sake of clearness, to state that the surface is an unduloid or nodoid according as β is positive or negative, *i. e.* according as $\pi/2>\theta>-\pi/2$ or $3\pi/2>\theta>\pi/2$.

If θ be supposed to vary continuously, and if one at least of the quantities α and β is finite, the form of the surface may be made to pass through a continuous cycle of changes.

Thus, between $\theta=0$ and $\theta=\pi/2$ the surface is an unduloid, the limits being the cylinder when $\theta=0$, and the sphere when $\theta=\pi/2$. As θ passes through the next quadrant the surface is a nodoid, the limits being the sphere, and a circle the plane of which is perpendicular to the axis of revolution, which is, as Plateau points out, a purely mathematical limit. In the third quadrant the surface is again a nodoid, the limits of which are the circle and catenoid. Finally, when θ lies between $3\pi/2$ and 2π the surface is an unduloid, the limits of which are the catenoid and the cylinder.

If now 2X and 2Y are the distance between and diameter of the rings respectively, and if ϕ_1 is the value of ϕ when $y=\mathrm{Y}$, we have

$$\mathrm{X}=\alpha\mathrm{E}+\beta\mathrm{F}, \quad \mathrm{Y}^2=\alpha^2\cos^2\phi_1+\beta^2\sin^2\phi_1.$$

Hence if α, β, and ϕ_1 vary, but so that X and Y are unaltered, we have, by differentiation,

$$\begin{aligned}\left\{\mathrm{E}-\frac{\beta^2}{\alpha^2}\int_0^{\phi_1}\frac{\sin^2\phi}{\Delta}d\phi+\frac{\beta^3}{\alpha^3}\int_0^{\phi_1}\frac{\sin^2\phi}{\Delta^3}d\phi\right\}\delta\alpha&\\ +\left\{\frac{\beta}{\alpha}\int_0^{\phi_1}\frac{\sin^2\phi}{\Delta}d\phi+\mathrm{F}-\frac{\beta^2}{\alpha^2}\int_0^{\phi_1}\frac{\sin^2\phi}{\Delta^3}d\phi\right\}\delta\beta&\\ +\left\{\alpha\Delta_1+\frac{\beta}{\Delta_1}\right\}\delta\phi_1=0, \quad . \quad . \quad . \quad . \quad . \quad . \quad . &\quad (3)\end{aligned}$$

and

$$2\alpha\cos^2\phi_1\delta\alpha+2\beta\sin^2\phi_1\delta\beta-(\alpha^2-\beta^2)\sin 2\phi_1\delta\phi_1=0. \quad . \quad (4)$$

But

$$\int\frac{\sin^2\phi}{\Delta}d\phi=\frac{\mathrm{F}-\mathrm{E}}{\kappa^2}, \quad \int\frac{\sin^2\phi}{\Delta^3}d\phi=\frac{1}{\kappa^2}\left\{\int\frac{d\phi}{\Delta^3}-\mathrm{F}\right\},$$

$$\int\frac{d\phi}{\Delta^3}=\frac{\alpha^2}{\beta^2}\left\{\mathrm{E}-\frac{\kappa^2\sin\phi_1\cos\phi_1}{\Delta_1}\right\}. \quad . \quad . \quad (5)$$

Substituting these values in (3) and (4) and eliminating $\delta\phi_1$ between them we get

$$\left.\begin{aligned}(\alpha^2\mathrm{E}-\beta^2\mathrm{F}+\alpha^2\Delta_1\cot\phi_1)\delta\alpha+\alpha^2(\mathrm{F}-\mathrm{E}+\Delta_1\tan\phi_1)\delta\beta=0,\\ \text{or} \qquad \mathrm{A}\delta\alpha+\mathrm{B}\delta\beta=0.\end{aligned}\right\}(6)$$

Now the mean curvature of a surface of revolution of minimum area has been proved by Lindelöf to be the same as that of a circle of radius $(\alpha+\beta)$. Hence

$$\frac{1}{2}\delta\left(\frac{1}{\mathrm{R}}+\frac{1}{\mathrm{R}'}\right)=-\frac{\delta\alpha+\delta\beta}{(\alpha+\beta)^2}$$

$$=\frac{\mathrm{A}-\mathrm{B}}{\mathrm{B}}\cdot\frac{\delta\alpha}{(\alpha+\beta)^2}=-\frac{\mathrm{A}-\mathrm{B}}{\mathrm{A}}\cdot\frac{\delta\beta}{(\alpha+\beta)^2}.$$

Hence the mean curvature has in general a critical value when $\mathrm{A}-\mathrm{B}=0$.

First confining ourselves to the case in which the principal ordinate is a maximum, and ϕ_1 and θ are less than

$\pi/2$, it is evident that, since F is always > E, B is always positive.

Also, by (5),

$$\frac{1}{\kappa}\frac{dF}{d\kappa}=\int\frac{\sin^2\phi}{\Delta^3}d\phi=\frac{1}{\beta^2\kappa^2}\left\{\alpha^2E-\beta^2F-\alpha^2\kappa^2\frac{\sin\phi_1\cos\phi_1}{\Delta_1}\right\};$$

whence, since $dF/d\kappa$ is positive and $\sin\phi_1\cos\phi_1$ is positive, $\alpha^2E-\beta^2F$ is positive, and therefore A is positive also. Further, B can only vanish if $\phi_1=0$; and none of the terms in A or B become infinite unless $\phi_1=0$ or $\pi/2$, cases which it will be seen hereafter it is unnecessary to consider.

Thus,

$$(A-B)/\alpha^2=2E-F(1+\cos^2\theta)+2\Delta_1\cot 2\phi_1=0 \quad . \quad (7)$$

is a relation which must be satisfied by ϕ_1 and θ when the mean curvature has a critical value for changes in the form of the surface which take place, subject to the conditions that the radii of the rings and the distance between them are constant.

Corresponding values of ϕ_1 and θ must be found by trial; but it will now be shown that if such a pair of values is known, when $\pi/2>\theta>0$, the values of ϕ_1 which are proper to $\pi-\theta$, $\pi+\theta$, and $2\pi-\theta$ can be readily deduced without further trials.

In the first place it is evident that, since the squares of the sine and cosine of θ alone enter into (7), the curve obtained by plotting the values of θ as abscissæ and those of ϕ_1 as ordinates is symmetrical with respect to the ordinate $\theta=\pi/2$, and that the same value of ϕ_1 corresponds both to θ and $\pi-\theta$.

If, then, we conceive a film attached to two rings, the volume and length of which vary continuously in such a way that (7) is always satisfied, as the cylinder changes to the sphere and thus to a nodoid forms which correspond to the same value of $\sin^2\theta$ will have the same value of ϕ_1 also, and the lengths will be given by the expression

$$X=\alpha(E+\cos\theta F)\ ; \quad . \quad . \quad . \quad . \quad . \quad (8)$$

where θ is $<\pi/2$ for the unduloid and $>\pi/2$, but $<\pi$ for the nodoid.

All these forms will have a maximum diameter half way between the rings. If we now proceed to discuss cases where the principal ordinate is a minimum, we must all through the previous investigation consider the lower limit of the integrals to be $\pi/2$ instead of 0, and ϕ_1 to be $>\pi/2$. With this convention no change is produced in any of the equations; as in equations (5) the quantities which are brought outside the sign of integration vanish, both when $\phi_1=0$ and when $\phi_1=\pi/2$.

Thus, writing as usual E_1 and F_1 for the complete integrals, and taking ϕ' instead of ϕ_1 as the upper limit of E and F, where ϕ' is $>\pi/2$, we have

$$2(E-E_1)-(F-F_1)(1+\cos^2\theta)+2\Delta(\phi')\cot 2\phi'=0. \quad (9)$$

Let ψ be an angle such that

$$F(\phi')-F_1=F(\psi);$$

then, by the addition theorem,

$$E(\phi')-E_1=E(\psi)-\sin^2\theta\sin\phi'\sin\psi.$$

Also

$$\tan\phi'\tan\psi=-\sec\theta,$$
$$\sin\phi'=\cos\psi/\Delta(\psi),$$
$$\Delta(\phi')\Delta(\psi)=\cos\theta,$$

and

$$\cot 2\phi'=\frac{1-\cos^2\theta\tan^2\psi}{2\cos\theta\tan\psi}.$$

Hence, substituting in (9),

$$2E(\psi)-F(\psi)(1+\cos^2\theta)-2\sin^2\theta\frac{\cos\psi\sin\psi}{\Delta(\psi)}$$
$$+2\frac{\cos\theta}{\Delta(\psi)}\times\frac{1-\cos^2\theta\tan^2\psi}{2\cos\theta\tan\psi}=0;$$

or

$$2E(\psi)-F(\psi)(1+\cos^2\theta)+2\Delta(\psi)\cot 2\psi=0, \quad . \quad (10)$$

which is the same as (7).

We thus conclude that, for every angle ψ or ϕ_1 which satisfies (7), there is a corresponding angle ϕ' which satisfies (9) for the same value of κ^2, and that these angles are connected by the relation

$$\tan\phi'\tan\phi_1=-\sec\theta. \quad . \quad . \quad . \quad . \quad (11)$$

If, then, we determine from (7) the values of ϕ_1 which correspond to certain values of θ between 0 and $\pi/2$, we can by (11) find the values of ϕ' corresponding to values between $3\pi/2$ and 2π; whence, since (7) and (9) depend on the squares of the sine and cosine of θ, the values of ϕ and ϕ' between $\pi/2$ and $3\pi/2$ are also known.

Before making any numerical calculations it is convenient to discuss (7) more fully.

Differentiating, we get

$$\sin 2\theta\left\{-\int_0^{\phi_1}\frac{\sin^2\phi}{\Delta}d\phi-\frac{1+\cos^2\theta}{2}\int_0^{\phi_1}\frac{\sin^2\phi}{\Delta^3}d\phi+\mathrm{F}\right.$$
$$\left.-\frac{\sin^2\phi_1\cot 2\phi_1}{\Delta_1}\right\}\delta\theta+\left\{2\Delta_1-\frac{1+\cos^2\theta}{\Delta_1}\right.$$
$$\left.-\frac{\sin^2\theta\cos 2\phi_1}{\Delta_1}-4\Delta_1\operatorname{cosec}^2 2\phi_1\right\}\delta\phi_1=0\,;$$

which, if we use equations (5) and simplify, becomes

$$\tan\theta\{\mathrm{E}-\mathrm{F}\cos^2\theta-\Delta_1\tan\phi_1\}\delta\theta+4\Delta_1\operatorname{cosec}^2 2\phi_1\delta\phi_1=0. \quad (12)$$

Hence $\delta\phi_1=0$ if $\theta=n\pi$, and if $\phi_1=n\pi/2$. Also, considering the case in which

$$\mathrm{E}-\mathrm{F}\cos^2\theta-\Delta_1\tan\phi_1=0, \quad . \quad . \quad . \quad . \quad (13)$$

we notice that, if we subtract (13) from (7), we get

$$\mathrm{E}-\mathrm{F}+\Delta_1\cot\phi_1=0; \quad . \quad . \quad . \quad . \quad . \quad (14)$$

and these equations are satisfied if $\theta=\pi/2$ and $\phi_1=56° 28'$.

For, if $\theta=\pi/2$, (13) is true identically, and (14) reduces to

$$\log_e\tan\left(\frac{\pi}{4}+\frac{\phi_1}{2}\right)=\operatorname{cosec}\phi_1,$$

which holds good when $\phi_1=56° 28'$.

Hence, when $\theta=\pi/2$, $\delta\phi_1/\delta\theta$ is of the form $\infty\times 0$, which is readily shown to be equal to zero.

To find the corresponding value of $\delta\phi'/\delta\theta$, we have from (11),

$$\sec^2\phi_1\tan\phi'\frac{d\phi_1}{d\theta}+\sec^2\phi'\tan\phi_1\frac{d\phi'}{d\theta}=-\sin\theta\sec^2\theta;$$

and by substituting from (11) for $\tan\phi'$ and $\sec^2\phi'$, this becomes

$$-\cos\theta\frac{d\phi_1}{d\theta}+\Delta_1^{\,2}\frac{d\phi'}{d\theta}=-\frac{\sin\theta\sin 2\phi_1}{2}.$$

Putting $\theta=\pi/2$,

$$\frac{d\phi'}{d\theta}=-\tan\phi_1=-\tan 56° 28'.$$

It must be remembered that θ corresponds to ϕ_1 and that if θ' corresponds to ϕ', $\theta'=2\pi-\theta$, so that $d\phi'/d\theta'=-d\phi'/d\theta$.

The question as to whether the critical value is a maximum or minimum has not yet been discussed. Since $\mathrm{A}-\mathrm{B}=0$, this depends on the sign of $\dfrac{d(\mathrm{A}-\mathrm{B})}{d\alpha}$; or, if we write $\mathrm{a}=\mathrm{A}/\alpha^2$, $\mathrm{b}=\mathrm{B}/\alpha^2$, upon that of $\dfrac{d}{d\alpha}(\mathrm{a}-\mathrm{b})$, where a and b are explicitly functions of θ and ϕ_1 only. Now, putting $\mathrm{a}-\mathrm{b}=\chi$,

$$\frac{d}{d\alpha}(\mathrm{a}-\mathrm{b})=\frac{d\chi}{d\alpha}=\left(\frac{d\chi}{d\theta}\right)\frac{d\theta}{d\alpha}+\left(\frac{d\chi}{d\phi_1}\right)\frac{d\phi_1}{d\alpha},$$

where $\left(\dfrac{d\chi}{d\theta}\right)$ and $\left(\dfrac{d\chi}{d\phi_1}\right)$ are the coefficients of $\delta\theta_1$ and $\delta\phi_1$, in (12), with the signs changed.

But since $\mathrm{A}=\mathrm{B}$, $d\beta/d\alpha=-1$, from (6). Hence, since $\cos\theta=\beta/\alpha$,

$$\sin\theta\,\frac{d\theta}{d\alpha}=\frac{\alpha+\beta}{\alpha^2}.$$

In like manner, from (4),

$$\frac{d\phi_1}{d\alpha}=\frac{2(\alpha\cos^2\phi_1-\beta\sin^2\phi_1)}{(\alpha^2-\beta^2)\sin 2\phi_1},$$

so that

$$\frac{d\chi}{d\alpha}=\left(\frac{d\chi}{d\theta}\right)\frac{\alpha+\beta}{\alpha^2\sin\theta}+2\left(\frac{d\chi}{d\phi_1}\right)\frac{\alpha\cos^2\phi_1-\beta\sin^2\phi_1}{(\alpha^2-\beta^2)\sin 2\phi_1}.$$

Now as we pass from one surface which satisfies the condition $\mathrm{A}-\mathrm{B}=0$ to another, the value of X changes; and it can easily be shown that if $d\mathrm{X}/d\theta$ be calculated subject to this condition, it is of the same sign as $d\chi/d\alpha$. Hence if X increases with θ, $d\chi/d\alpha$ is positive and the critical value is a minimum; if X diminishes as θ increases, it is a maximum. If X is a maximum or minimum the curvature has a stationary value, but it is not itself a maximum or minimum.

I have calculated by trial the values of ϕ_1 which satisfy (7) for a few angles between 0° and 90°. They are given, together with the corresponding values of E, F, and Δ_1, in Table I.

TABLE I.

θ.	ϕ_1.	E.	F.	Δ_1.
0°	45°·00	0·785	0·785	1·000
10	45·23	0·787	0·792	0·992
30	46·94	0·799	0·841	0·931
45	49·28	0·812	0·913	0·844
60	52·25	0·824	1·018	0·729
80	55·84	0·833	1·169	0·580
90	56·47	0·834	1·200	0·552

The values in the last four columns are repeated in the reverse order as θ increases from 90° to 180°.

In the next Table are given the values of $\phi''=\pi-\phi'$, and of $E_1-E(\phi'')$ and $F_1-F(\phi'')$. In representing the results graphically it is best to take $\phi'-\pi/2$ or ϕ_2, as corresponding to ϕ_1, and therefore these values are also given.

TABLE II.

θ.	ϕ''.	ϕ_2.	$E_1-E(\phi'')$.	$F_1-F(\phi'')$.
360°	45°·00	45°·00	0·785	0·785
350	45·20	44·80	0·772	0·792
330	47·20	42·80	0·664	0·841
315	50·60	39·40	0·519	0·913
300	57·15	32·85	0·326	1·018
280	75·65	14·35	0·055	1·169
270	90·00	0·00	0·000	1·200

The values of $\Delta(\phi')$ are omitted because they are readily obtained by the formula $\Delta(\phi')\Delta(\phi_1)=\cos\theta$.

The curve obtained by means of these Tables, which shows the relation between ϕ_1 or ϕ_2 and θ, is given in fig. I.

Rectangular coordinates are perhaps the most convenient; but if θ and ϕ be regarded as angle and radius vector, the curve assumes the symmetrical form shown in fig. II.

This result completes the solution of the problem; but the nature of the conclusions at which we have arrived is more evident if we proceed to deduce the ratios of the lengths and principal diameters of the films to the radii of the rings.

This is done by means of the following relations, where symbols with unity subscript refer to bulging films, and those with 2 subscript to films the principal ordinate of which is a minimum.

$$\alpha_1/Y=1/\Delta_1,$$
$$X_1/\alpha_1=E+F\cos\theta;$$

whence X_1/Y is found.

$$\beta_2/Y=\alpha_2\cos\theta/Y=\cos\theta/\Delta_2=\Delta_1,$$
$$X_2/\beta_2=(E'-E_1)\sec\theta+(F'-F_1);$$

whence X_2/Y is obtained.

It is evident from these equations that $\alpha_1\beta_2=Y^2$; *i. e.* the radius of the rings is a mean proportional between the principal ordinates of two surfaces in which the modulus of the elliptic integrals is the same, and the principal ordinates of which are a maximum and a minimum respectively.

Table III.

θ.	α_1 Y.	X/α_1.	X/Y.	θ.	β_2/Y.	X/β_2.	X/Y.
0°	1·000	1·571	1·571	180	1·000	0·000	0·000
10	1·008	1·567	1·579	190	0·992	0·008	0·008
30	1·074	1·527	1·640	210	0·931	0·073	0·068
45	1·184	1·458	1·726	225	0·844	0·179	0·151
60	1·372	1·333	1·829	240	0·729	0·366	0·267
80	1·725	1·036	1·787	260	0·580	0·852	0·494
90	1·810	0·834	1·509	270	0·552	1·200	0·663
100	1·725	0·630	1·086	280	0·580	1·486	0·862
120	1·372	0·316	0·433	300	0·729	1·671	1·218
135	1·184	0·166	0·196	315	0·844	1·647	1·391
150	1·074	0·071	0·076	330	0·931	1·607	1·495
170	1·008	0·008	0·008	350	0·992	1·576	1·563
180	1·000	0·000	0·000	360	1·000	1·571	1·571

The "march" of the functions is shown by means of the curves in figs. III., IV., and V. Thus, if p be the length of the principal ordinate (whether it be a maximum or a minimum), fig. III. shows the relation between p/Y and θ, fig. IV. that between X/p and θ, and fig. V. that between X/Y and θ.

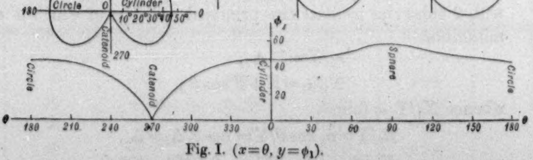

Fig. I. ($x=\theta$, $y=\phi_1$).

By plotting the values of X Y we find that the maximum occurs when $\theta=70°$. The corresponding value of ϕ_1 is 54°·15, and this gives

$$\alpha/Y=1{\cdot}545, \quad X/\alpha=1{\cdot}2044, \quad X/Y=1{\cdot}860.$$

If, then, we suppose the rings to approach to or recede from each other, and the volume and diameter of the film to be at the same time altered so that it always satisfies the conditions of critical mean curvature, it will undergo the following changes of form.

Starting with the rings in contact, and supposing that as they separate the film has a slight bulge, it will first be a nodoid, and the length and principal diameter will increase together. When the length is a little more than one and a half (1·509) diameters of the rings the film is spherical, and the principal diameter is then a maximum ($\alpha/Y=1{\cdot}810$). As the diameter begins to decrease the film becomes an unduloid, but the length increases until it is 1·860 × diameter of rings. Thereafter length and diameter decrease together until, when the latter is a third proportional to the diameters of the sphere and of the rings, it reaches its minimum value ($\beta/Y=0{\cdot}552$). The film is then a catenoid. As the length diminishes it becomes a nodoid, exerting a negative or outward pressure, and this continues until the cycle is completed by the rings meeting again.

The whole of the above investigation has taken place subject to the condition that $\phi_1<\pi/2$, and without reference to the stability of the films, which is, however, secured by the condition as to ϕ_1 except in the neighbourhood of $\theta=180°$.

The curves, when drawn on a larger scale, lend themselves to the solution of a number of problems with an accuracy quite sufficient for practical purposes.

Thus, if we wish to determine the conditions of the film which has a critical curvature when the principal diameter or the length is a given multiple of the diameter of the rings, we have only to draw a circle with the origin in figs. III. or V. as the centre, and with the radius equal to the given ratio. The points of intersection give the value of θ; ϕ_1 is found from fig. II.; and thus the other quantities can be determined either by calculation or by means of the other figures.

It is evident, since the maximum radius of the curve in fig. V. is such that $X/Y=1{\cdot}860$, that the curvature cannot have a critical value for films such that the ratio of the length to the diameter of the rings exceeds this number, while for all less ratios there must be two critical points, a maximum and a minimum respectively.

If, then, we suppose a film attached to two rings to be initially a nodoid with a diameter exceeding that of the sphere, and to contract gradually, its behaviour, as regards change of curvature, within the limits of the problem, would be as follows.

If the length were $>1{\cdot}860 \times$ diameter of rings, the film, after becoming a sphere, would always be an unduloid until it reached the limit at which the conditions no longer apply. The mean curvature would increase as the principal diameter diminished.

If $1{\cdot}860 > X/Y > 0{\cdot}663$, the film remains an unduloid throughout all stages after it has become a sphere; but the mean curvature first increases, then diminishes, and finally increases again. The cylinder is the form of minimum mean curvature if $X/Y = 1{\cdot}571$. The sphere is the form of maximum curvature if $X/Y = 1{\cdot}509$.

If $X/Y = 0{\cdot}663$ the last series of statements holds good, with the addition that the minimum mean curvature is zero. Hence the surface passes through the form of the limiting catenoid, which is such that no catenoid can be formed between the rings if the distance between them is increased. If the distance between the rings is diminished, two catenoids pass through them.

If $X/Y < 0{\cdot}663$, the maximum mean curvature which is attained while the film is still a nodoid diminishes as the figure passes through the forms of the sphere, cylinder, and catenoid, and then becomes negative, *i. e.* the pressure exerted by the film is directed outwards. The minimum is reached when the form of the film lies between the two catenoids which can be drawn through the rings.

The calculations enable us also to solve another problem. If the interiors of two similar films be connected which are formed between equal and equidistant rings, and which are stable when separated from each other, the system will only be in stable equilibrium if a contraction in the principal ordinate, producing a decrease in volume, is attended by a decrease in the curvature.

Hence no pair of similar films so arranged can be in stable equilibrium if the length is $>1{\cdot}860\times$ diameter of rings.

Two cylinders cannot be in stable equilibrium if the length is $>\frac{\pi}{2}\times$ diameter, nor two spheres if the length is $>1{\cdot}509\times$ diameter of rings, *i. e.* $>0{\cdot}834\times$ diameter of sphere.

XXI. *Influence of Change of Condition from the Liquid to the Solid State on Vapour-pressure.* *By* W. RAMSAY, *Ph.D.*, *and* SYDNEY YOUNG, *D.Sc.*[*]

IN Wiedemann's *Annalen*, vol. xxviii. p. 400, W. Fischer has published a paper on the above subject. After stating, in the course of a historical sketch, that no experimental work with a view to decide whether the vapour-pressure of a solid is identical with that of its liquid at the same temperature below the melting-point of the solid has been carried out since Regnault's time, he corrects himself in a footnote in which he refers to a paper published by us on this subject in the Philosophical Transactions in 1884. He there states, however, that he gained a prize through some work on the vapour-pressures of water and of benzene in 1883. Now it is generally understood that priority is determined, not by the date at which work is done, but by the date of publication; and as Fischer's work was not made public until July 1886, there can be no question of priority between us. But in the short sentence on our work he commits a grave error in stating that our work was merely qualitative; on the contrary, it was rigorously quantitative; and we then showed that the numbers calculated for the vapour-pressure of ice, using as data an extension of the vapour-pressures of water below 0°, extrapolated from Regnault's measurements above 0°, his determinations of the heat of vaporization of water and fusion of ice, and of the specific heat of ice, agreed closely with those found by us. As regards benzene, however, our work had no pretence to be quantitative.

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[*] Read December 11, 1886.

Fischer's experiments were made by a process identical in principle with that employed by Regnault. The water, or benzene, on which he experimented, was introduced, by a process well devised for excluding air, into a vacuum connected with a gauge, and on alterating the temperature of the liquid, alteration of pressure was noted and registered. His experimental results are very regular, and, so far as water and ice are concerned, confirm ours, and agree well with theory.

But although Fischer's experimental results with benzene are equally regular, yet they present certain anomalies which are difficult to explain. From his results he calculated constants—one series to represent the relations of the pressure of vapour in contact with liquid, and the other to represent similar relations for vapour in contact with solid, employing formulæ of the general form $p=a+bt+ct^2$. From the numbers calculated by means of these constants, he concluded that *the vapour-pressure of liquid benzene is not identical with that of solid benzene at the melting-point of the solid.* This conclusion is evidently opposed to the second law of thermodynamics; and, if it had not been apparently supported by Fischer's really excellent experimental measurements, might have been dismissed at once as absurd. But on revising Fischer's results, we find that the constants employed by him, if used to calculate the vapour-pressures of the solid at low temperatures, give results which are by no means in accordance with his measurements. Indeed at -8° the calculated pressure is 13·51 millim., whereas Fischer found 14·2 millim.; and it is evident, from a graphic representation of his results, that the divergence would increase at lower temperatures. Now it is known that the relations of pressure to temperature are better expressed by means of a formula of the type suggested by Biot, $\log p=a+b\alpha^t+c\beta^t$; or, for a small range of pressure, by the simpler form $\log p=a+b\alpha^t$. On calculating constants from Fischer's results by means of this formula, we found that while a curve was obtained agreeing better with his experimental results, the anomaly which he supposed (viz. want of coincidence at the melting-point) no longer existed. As in the case of water and ice, solid and liquid acetic acid, solid and liquid bromine, and solid and liquid iodine, which have formed the subject of our experiments (Phil. Trans. 1884, p. 461, and Trans. Chem. Soc. 1886, p. 453), solid and liquid benzene exert the same vapour-pressure at the melting-point.

For recalculating Fischer's results, his pressures at -7°, -2°, and $+3^{\circ}$ were taken. At -7°, the vapour-pressure of the solid determined by him was 15·273 millim.; at -2°, 21·679 millim.; and at $+3^{\circ}$, 30·324 millim. The constants are $a=4\cdot81664$; $\log b=0\cdot5602315$; $\log \alpha=\bar{1}\cdot99628446$; b is negative; and t = temperature centigrade $+7$. For the vapour-pressures of liquid benzene, Fischer's results agree well with his formula. As data are in existence whereby the vapour-pressures of solid benzene can be calculated for a short interval of temperature below the melting-point, provided those of the liquid are accurately known, it was deemed advisable to check Fischer's results with liquid benzene by the dynamical method already described by us (Trans. Chem. Soc. 1885, p. 42).

This was accordingly done. A large quantity of commercial benzene was distilled, and the first half, boiling within five degrees, was frozen twice, the liquid portion being poured off each time. The solid portion was then shaken repeatedly with sulphuric acid until the acid was no longer coloured, thiophene being thus removed. The remainder was shaken with water and dried, and then fractionated until a product of constant boiling-point was obtained. The actual boiling-point, at a pressure of 753·4 millim., was $79^{\circ}\cdot9$.

The following determinations with the liquid were made. At the lower temperature, thermometers graduated in $\frac{1}{10}$ divisions were employed. The zero-points of these thermometers, and the apparent lowering of temperature consequent on reduction of pressure, were determined, and corresponding corrections introduced. For higher temperatures (above 50°), a thermometer previously used for determination of vapour-pressures, and of which the corrections had been thoroughly investigated, was used. The three $\frac{1}{10}$ thermometers we shall name A, B, and C; the one used at higher temperatures, D.

Liquid Benzene.

Series I.		Series II.		Series III.	
Temp.	Pressure.	Temp.	Pressure.	Temp.	Pressure.
°	millim.	°	millim.	°	millim.
A. −1·84	24·0	A. 5·30	35·05	D. 31·4	125·85
−0·97	25·1	6·25	37·2	33·6	137·9
−0·02	26·8	7·03	38·45	35·5	150·8
+0·98	27·9	7·47	39·85	44·7	221·0
1·23	28·15	7·98	40·9	50·1	267·0
2·03	29·15	8·37	41·8	51·85	287·4
3·08	30·95	9·21	43·0	54·25	313·9
3·13	31·15	10·44	47·25	56·4	339·5
4·84	34·7	12·51	51·65	58·8	371·4
5·06	35·2	14·66	57·8	61·2	402·7
5·31	35·4	16·85	64·5	63·6	440·0
5·48	35·9	18·72	70·75	67·2	497·6
5·74	36·15	20·54	77·25	69·25	534·6
B. 5·63	36·15	22·97	85·5	71·85	582·0
A. 8·98	42·8	25·37	96·4	74·1	630·3
B. 8·77	42·8	28·15	109·35	76·65	684·6
		30·87	123·45	79·6	743·1
		38·78	173·0		
		39·35	174·95		
		41·41	190·8		
		43·71	209·6		
		45·97	230·0		
		47·94	249·1		
		49·36	263·3		

A curve was drawn to represent these relations; and from it three points were chosen, viz. 0°, 40°, and 80°; the corresponding pressures are: 0°, 26·54 millim.; 40°, 180·2 millim.; and 80°, 755·0 millim. The constants for the formula $\log p = a + b\alpha^t$ are

$$a = 4{\cdot}72452\,;\ \log b = 0{\cdot}5185950\,;\ \log \alpha = \bar{1}{\cdot}996847125\,;$$

b is negative.

The following Table shows the calculated vapour-pressure for each 10°.

Temperature.	Pressure.	Temperature.	Pressure.
°	millim.	°	millim.
−10	14·97	40	180·20
0	26·54	50	268·30
10	45·19	60	388·51
20	74·13	70	548·16
30	117·45	80	755·0

These numbers agree fairly well with Regnault's results at and above 10°. Below that temperature his constants are calculated from the vapour-pressures of the solid as well as of the liquid, and of course are therefore incorrect.

We give a Table of comparison of our calculated results, with those calculated by Fischer, between 0° and 6°.

Temp.	Pressure.		Temp.	Pressure.	
	F.	R. and Y.		F.	R. and Y.
°	millim.	millim.	°	millim.	millim.
0	26·40	26·54	4	32·84	32·99
1	27·87	28·04	5	34·68	34·80
2	29·43	29·61	6	36·60	36·69
3	31·10	31·26			

It will be seen that the agreement is a very close one; and as our determinations were made by the dynamical method, while Fischer's were obtained statically, there is a strong presumption that the substance in both cases was pure.

In order to calculate the vapour-pressures of solid from those of liquid benzene, the following formula was employed:—

$$\text{Vapour-pressure of solid at } (t-1) = P_t - (P'_t - P'_{t-})\left(\frac{V_{t-\frac{1}{2}} + F_{t-\frac{1}{2}}}{V_{t-\frac{1}{2}}}\right);$$

P = vapour-pressure of solid;
P' = vapour-pressure of liquid;
V = heat of vaporization of liquid;
F = heat of fusion of solid;
t = temperature of solid and liquid.

It is therefore necessary to know the heat of vaporization of liquid benzene at different temperatures, and the heat of fusion of solid benzene; and in order to calculate these, the specific heats of liquid and of solid benzene. The following determinations are available:—

1. *Heat of Vaporization of Liquid Benzene.*—Regnault (*Mémoires de l'Institut*, xxvi. p. 881) has determined the total heats of vaporization of benzene at different temperatures, while Schiff (*Annalen*, ccxxxiv. p. 344) has made a single

determination at the boiling-point. Regnault's formula is

$$H = a + bt + ct^2,$$

where $a=109$, $b=0{\cdot}24429$, and $c=-0{\cdot}0001315$. Schiff's single determination at the boiling-point, 80°·35, at a pressure of 765·1 millim., is 93·4 to 93·5 calories.

2. *Heats of Fusion of Solid Benzene.*—Peterson and Widmann (*J. prakt. Chem.* xxiv. p. 129) give the number 29·09 calories; and Fischer (*loc. cit.*) found 30·085 calories.

3. *Specific Heat of Liquid Benzene.*—This has been often observed. But isolated observations are for our purpose comparatively valueless, for the specific heat varies with the temperature. Formulæ are given only by Schüller (Pogg. *Ann.*, Ergänzungs-Band, p. 5), and by Schiff (*loc. cit.*). We have used Schiff's formula. It is, specific heat$=a+bt$; where $a=0{\cdot}3834$ and $b=0{\cdot}001043$. Between narrow limits of temperature this may be accepted as sufficiently correct.

4. *Specific Heat of Solid Benzene.*—Fischer (*loc. cit.*) gives 0·319.

Calculating the heat of vaporization at the boiling-point under normal pressure from Regnault's total heats of volatilization and Schiff's specific heat of liquid benzene, the number 93·67 is obtained; while Schiff found by direct measurement 93·4 to 93·5. This is a strong presumption in favour of the correctness of the data.

The mean of the two determinations of the heats of fusion of benzene was taken.

The following Table summarizes the data for calculating the vapour-pressures of the solid. But this calculation involves the assumption that the heat evolved on solidification at any low temperature is equal to that evolved at the ordinary melting-point, minus the product of the specific heat of the solid into the difference of temperature; and that the specific volume of the vapour in contact with solid is equal to that of vapour in contact with liquid. It is certain that neither of these assumptions is true; hence it is not legitimate to calculate the vapour-pressures of the solid from those of the liquid. Still, for some degrees below the melting-point, the error involved in these assumptions is probably not very great.

Temp.	P'.	$P'_t - P'_{t-1}$.	$V_{t-\frac{1}{2}}$.	$F_{t-\frac{1}{2}}$.	$\frac{V_{t-\frac{1}{2}}+F_{t-\frac{1}{2}}}{V_{t-\frac{1}{2}}}$.	$P_t - P_{t-1}$.	P.
°	mm.	mm.	calor.	calor.			mm.
5·58	35·89	1·86	108·3	29·4	1·271	2·365	35·89
4·58	34·03	1·78	108·4	29·1	1·268	2·258	33·52
3·58	32·25	1·69	108·5	28·8	1·265	2·139	31·27
2·58	30·56	1·62	108·6	28·5	1·262	2·045	29·13
1·58	28·94	1·54	108·8	28·2	1·260	1·941	27·08
0·58	27·40						25·14

The vapour-pressures of solid benzene, determined by our method, are given in the following Table. As Fischer's method was statical, while ours is dynamical, a comparison of the results of both is therefore given.

Pressure.	Temp.	Pressure.	Temp.	Pressure.	Temp.
SERIES I.		SERIES I. (cont.).		SERIES II. (cont.).	
millim.	°	millim.	°	millim.	°
35·9	+5·43	21·8	−0·95	14·0	− 7·02
35·4	5·21	21·4	−1·12	13·25	− 7·37
35·2	5·07	21·0	−1·45	13·10	− 7·53
34·7	4·89	19·95	−2·00	12·80	− 8·42
31·15	3·62	19·0	−2·54	11·6	− 8·77
30·95	3·32	19·0	−2·97	11·2	− 9·90
29·15	2·70	18·05	−2·98	10·2	− 9·72
29·15	2·75	16·3	−4·63	10·1	−10·54
28·7	2·41	16·25	−5·45	9·95	−11·03
28·15	2·21	13·8	−6·43	7·35	−14·12
27·9	1·99	12·35	−8·07	SERIES III.	
26·8	1·29				
26·7	1·33	SERIES II.		14·25	− 7·01
26·65	1·33			14·0	− 7·70
25·9	0·85	21·9	−1·26	10·4	−11·2
25·1	0·64	21·1	−1·60	10·2	−11·0
24·45	0·23	20·05	−2·61	10·2	−10·63
24·0	0·0	18·75	−3·08	9·95	−11·62
23·9	−0·03	17·15	−4·38	9·3	−11·92
22·75	−0·78	15·2	−5·78	9·3	−11·3
22·2	−0·91	15·0	−6·02	8·7	−12·12

For the first two series thermometers A and B were used; for Series III. another thermometer, D; and it will be seen that its readings confirm those of the other two. The individual results are not so concordant as Fischer's. The reason is that the volatilization of solid benzene is so quick as to make it difficult to obtain an accurate reading before the solid has volatilized and partially exposed the thermometer-bulb. These numbers, near the melting-point, show close concordance with those of Fischer, but at lower temperatures they show signs of divergence. For example at −8·42, if Biot's formula be applied, the difference between Fischer's results and ours amounts to 1·39 millim.; and it is evident, from the graphical representation, that the difference would be an increasing one. It is to be noted that Biot's formula agrees with Fischer's own results much better than the formula employed by him.

Our results were plotted on curve paper, and the constants for a formula calculated from points on a curve drawn to pass well through them. The constants for the formula $\log p = a + ba^t$ are

$$a = 4\cdot82602\ ;\ \log b = 0\cdot5784772\ ;\ \log \mathbf{a} = \bar{1}\cdot9959086;$$

$t = t^\circ$ Centig. $+10$; b is negative.

The following Table comprises (A) the values calculated from the vapour-pressures of the liquid; (B) those calculated from the formula and constants given by Fischer; (C) those calculated from Fischer's results by Biot's formula; and (D) those calculated from our results by Biot's formula.

Temperature.	A.	B.	C.	D.
°	millim.	millim.	millim.	millim.
5·58	35·89	35·62	35·85	35·86
4·58	33·52	33·36	33·62	33·39
3·58	31·27	31·42	31·50	31·07
2·58	29·13	29·54	29·50	28·90
1·58	27·08	27·73	27·61	26·85
0·58	25·14	25·97	25·82	24·94
−0·42	......	24·28	24·14	23·14
1·42	......	22·65	22·55	21·46
2·42	......	21·09	21·06	19·89
3·42	......	19·59	19·66	18·41
4·42	......	18·15	18·33	17·04
5·42	......	16·77	17·09	15·75
6·42	......	15·45	15·92	14·56
7·42	......	14·20	14·82	13·44
8·42	......	13·01	13·79	12·40
9·42	......	11·89	12·82	11·43
10·42	......	......	......	10·53
11·42	......	......	......	9·69
12·42	......	......	......	8·91

It is possible to calculate the heat of fusion of solid benzene, from the value of $\frac{dp}{dt}$ at the melting-point, from the equation

$$\frac{dp}{dt}(\text{solid}) \quad \frac{p}{dt}(\text{liquid}) = \frac{V+F}{V},$$

where V is the heat of vaporization at the melting-point, and F the heat of fusion.

With Fischer's formula and constants	. F = 6·29	calories
With Fischer's results and Biot's formula.	F = 21·1	„
With our results and Biot's formula . .	. F = 35·4	„
The number found by Fischer	. F = 30·085	„
The number found by Peterson and Widman	. F = 29·09	„

From these numbers it is evident that, although our constants are not perfectly correct, yet they agree better with experimental evidence than those of Fischer.

XXII. *On the Nature of Liquids, as shown by a Study of the Thermal Properties of Stable and Dissociable Bodies.* *By* WILLIAM RAMSAY, *Ph.D., and* SYDNEY YOUNG, *D.Sc.*[*]

THE fundamental concept of Chemistry, as well as of Physics, is the molecular and atomic constitution of matter. This concept serves to represent to the chemist the definite composition of compounds, and, to some degree, the nature of isomerism, while all attempts to realize and explain the progress of chemical change depend on its adoption. This concept also furnishes to the physicist the means of conceiving the relations of heat, light, magnetism and electricity to matter ; and where the action of one of these agents involves not merely a change in the form, but also in the nature of the matter, the problem becomes of deep interest to both chemist and physicist. The action of heat on matter, from the physical side, involves an increased molecular motion, tending to separate individual molecules from each other, on the one hand ; or, on the other, if this separation be opposed by confining walls, to increase the momentum and number of impacts on those walls, and therefore to raise the pressure. But this increased molecular motion is accompanied by greater internal vibration, which eventually leads, in almost all cases, to a simplification or rearrangement of the molecules, involving chemical change. When increased molecular motion is imparted to gases at temperatures much above their points of condensation, and at moderate pressures, the problem is a comparatively simple one; and has been solved with great success by Clausius, Maxwell, Thomson, and others, from the physical side, and from the chemical side by Pfaundler, Naumann, and Willard Gibbs. But near their condensing points, and also at high pressures, Boyle's and Gay-Lussac's laws no longer hold, owing partly no doubt to the mutual attraction of the molecules, and also to the fact that the absolute size of the molecules is no longer insignificant relatively to the space which they occupy. Both these causes of deviation may be relegated to the class "physical," inasmuch as the mutual attraction alluded to is not confined to any small number of molecules, but is exercised by each molecule on all its neighbours, and limited in absolute amount only by the relative masses of the attracting molecules and by their distances from each other. But it is also conceivable that this attraction may be wholly or in part of a chemical nature, tending towards the formation of complex molecules, resulting from combination of two or more simple molecules. Now as this deviation from the simple gaseous laws occurs both with what are commonly termed "stable" and with "dissociable" substances, it is of importance to enquire whether the abnormality of the vapour-density of stable substances is at all due to chemical association of molecules; and how much of the abnormality of dissociable substances is to be ascribed to purely physical attraction of the molecules for each other, due to mere propinquity.

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[*] Read December 11, 1886.

At any temperature below the critical one, when the volume of gas is decreased, pressure rises until a certain maximum is attained, when it becomes constant, and change of state occurs. It is conceivable, on the one hand, that the liquid condition is a purely physical one, and that a liquid consists of molecules similar in all respects to those of its gas, but, owing to their closer proximity, exhibiting that form of attraction which is known as cohesion. And on the other hand, it has been advanced by Naumann and others that the gaseous molecules, in changing to liquid, form molecular groups of definite complexity, exercising cohesive attraction on each other; and, according to this view, the problem is both a physical and a chemical one. According to the first view, if heat be imparted to a liquid, work is done in expansion against pressure, and in overcoming cohesion; and, according to the second view, additional work is done in dissociating the complex molecules into their simpler constituents, and in imparting increased velocity and internal motion to those constituent molecules (see "Evaporation and Dissociation," part i., Trans. Roy. Soc. 1886, Part I.).

When a substance, such as chloral hydrate or ammonium chloride, passes from the solid or liquid into the gaseous state, the physical change is obviously accompanied by a chemical one, for dissociation into simpler molecules occurs. There is an obvious analogy between evaporation and such cases of dissociation; and we have recently undertaken experimental work to test whether this analogy is a real one.

In part i. of this series of papers the phenomena attending the volatilization of such solids as dissociate wholly or partially on their passage from the solid to the gaseous state have been studied. There are two ways of measuring the vapour-pressure of a stable substance, which have been termed by Regnault the statical and the dynamical respectively. The first consists in measuring the pressure exercised by the vapour of the substance kept at a uniform temperature; and the second in measuring the highest temperature attainable by the substance at given pressures, when evaporation freely takes place. It has been shown by Regnault, and by numerous other observers, that these methods give identical results with liquids, and by ourselves with solids (Trans. Roy. Soc. Part I. 1884, p. 37). But in the case of the majority of the dissociable bodies examined, the results of the two methods were not identical; indeed, in many cases in which dissociation is complete, or nearly so, the temperature of volatilization is independent of pressure. With nitrogen peroxide, acetic acid, and ammonium chloride, however, the two methods gave identical results. This method, therefore, cannot be regarded as a means of deciding the question of the analogy between evaporation and dissociation, unless, indeed, two kinds of chemical combination be conceived, one of which may be termed "molecular combination" as distinguished from "atomic combination."

In parts ii. and iii. the thermal behaviour of stable liquids has been investigated, as exemplified by alcohol and ether. For a complete account of these researches reference must be made to the original papers (Trans. Roy. Soc. 1886, Part I.*). We are here concerned chiefly with the densities of the saturated vapours, and with the heats of vaporization. We found, with alcohol, that the density of the saturated vapour was normal at temperatures below 40° or 50°, and remained normal down to a temperature of 13°, the lowest temperature at which observations could be made. With ether the vapour-density was approaching normality at 13°, and from the form of the curve would have doubtless become normal at a lower temperature. In both cases, with increase of temperature and corresponding increase of pressure, the density of the saturated vapour increased towards the critical point with great rapidity, until at the critical point the weight of unit volume of the saturated vapour was equal to that of the liquid.

At the critical point the heat of vaporization of a stable liquid is theoretically zero; below that temperature we found it to increase with alcohol and with ether as the temperature fell; with ether the increase was found to be continuous to the lowest observed temperature 13°; whereas, with alcohol, it becomes practically constant below about 20°. Our calculated numbers correspond well with direct measurements by various observers at the boiling-points under atmospheric pressure.

With acetic acid the results were very different. With rise of temperature above 150° the density of the saturated vapour increased, as with other liquids; but below that temperature (at which the vapour-density was 50·06, the calculated density being 30) the vapour-density, instead of continuing to fall, rose more and more rapidly with fall of temperature, until at 20° the vapour-density was approximately 59, and apparently, from the form of the curve, was continuing to rise more and more rapidly, with fall of temperature (see figs. 2 & 3). It may be mentioned that direct observations by Bineau at 20° give nearly the same value.

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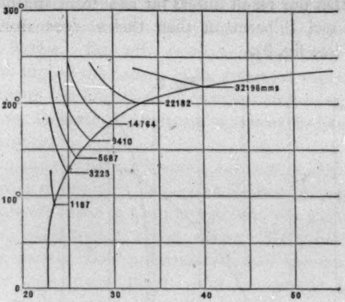
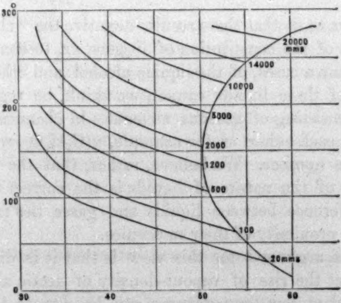
* The constants for ether will be published shortly.

Fig. 1.



Vapour-density (H = 1 at t° and p millim.).
Alcohol.

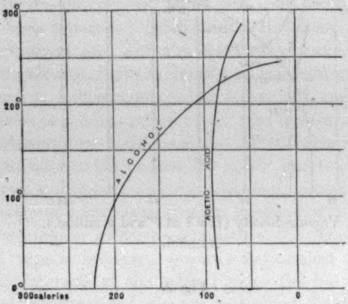
Fig. 2.



Vapour-density (H = 1 at t° and p millim.).
Acetic Acid.

The curve representing heats of vaporization of acetic acid at various temperatures also differs entirely in form from those of alcohol and ether, for it exhibits a maximum at 110°, and decreases both with rise and with fall of temperature. It is difficult to draw any conclusion from a comparison of our measurements of this quantity at the boiling-point under atmospheric pressure with those of other observers; but it may be stated that our result differs far less from the observation of Favre and Silbermann than theirs does from that of Berthelot (see fig. 3).

Fig. 3.



It appears to us that these results negative the "chemical" explanation of the constitution of liquids, or, to confine ourselves to known cases, of the liquids alcohol and ether. The molecules of these liquids cannot, we think, be regarded as complex, consisting of gaseous molecules in chemical combination with each other, as, for example, $n(C_2H_6O)$, where n is any definite number. We believe, rather, that the physical explanation of the nature of liquids is the correct one, and that the difference between liquids and gases lies merely in the relative proximity of their molecules.

The chief argument for this view is that it is difficult to conceive that the rise of vapour-density of acetic acid, both at high and at low temperatures, can be due to the same cause, under conditions so radically different; for at high temperatures we have conditions unfavourable to chemical combination, but owing to the necessarily high pressure, the molecules are in close proximity; whereas, at low temperatures, the conditions are favourable to chemical combination, while the molecules, owing to the corresponding low pressures, are very far apart. Now we have shown that, with alcohol and with ether, a rise of density does not accompany fall of temperature ; indeed, the saturated vapour of alcohol, at low temperatures, obeys the laws of Boyle and Gay-Lussac; while the rise of vapour-density at high temperatures is common to all bodies. But with acetic acid, the lower the temperature the higher the density of its saturated vapour—a fact which indicates the formation of complex molecules ; at high temperatures, however, it forms no exception in behaviour to ordinary liquids.

We have shown that with stable substances there is proof of the absence of complex molecules in their vapours ; but it might be asserted that in the passage from the gaseous to the liquid state, combination might occur. That this cannot be the case, is evident from a consideration of the behaviour of liquids near their critical point. For the specific volumes of liquid and gas just below the critical point are nearly equal; and were the liquid to consist of congeries of gaseous molecules, there would necessarily be fewer molecules in unit volume of the liquid than in unit volume of the gas—an improbable conception.

It is impossible to decide from our experiments whether the higher limit of vapour-density of acetic acid is 60 ; and the difficulty of measuring small pressures with sufficient accuracy renders an answer to this question apparently impossible ; but it is a remarkable circumstance that our observations, as well as those of Bineau, should so closely approximate to this limit. Although the curves representing the density of the saturated vapour in figs. 1 and 2 apparently point to a vapour-density greater than 60, yet a trend in the curve is not impossible ; and it is conceivable that at lower temperatures than those represented, the density might remain normal for $C_4H_8O_4$.

If there is a definite limit to the vapour-density of acetic acid, then the following considerations will hold. It has been pointed out in our paper on acetic acid, that condensation took place before pressure ceased to rise ; and the same phenomenon was observed with chloral ethyl-alcoholate, where dissociation is known to occur. Now with alcohol and with ether absolutely no sign of this behaviour was observable; condensation occurred the moment the vapour-pressure was reached, but not till then. This behaviour corresponds to that of a mixture. If an indifferent gas, to take an extreme instance, is compressed along with the vapour of a condensable liquid, pressure continues to rise after condensation has commenced, until the gas, if possible, has been dissolved, or has itself condensed. On the other hand, if a small quantity of liquid of high boiling-point be present along with a large quantity of liquid of low boiling-point, the liquid of higher boiling-point separates out first, on reduction of volume, while pressure continues to rise. This was indeed noticed with an impure sample of ether; and the absence of this behaviour affords proof of the homogeneity of a liquid.

Supposing the vapour of acetic acid to consist of molecules of two different degrees of complexity, it is probable that the more complex would be first condensed, and that pressure would rise until the less complex molecules had also condensed. This was in fact observed. But below a certain temperature the substance would consist almost wholly of more complex molecules, and the phenomenon would then be less visible. This is indeed the case with the isothermals at 50° and at 78°·4. At higher temperatures the phenomenon becomes evident. That this behaviour is not the effect of impurity has been proved by the fact that the vapour-pressures at low temperatures, measured by the statical and by the dynamical methods, were identical.

Formulæ representing the dependence of dissociation on pressure and temperature have been proposed from thermodynamical considerations by Prof. Willard Gibbs*. The formula is for acetic acid

$$\log \frac{2{\cdot}073(\mathrm{D}-2{\cdot}073)}{(4{\cdot}146-\mathrm{D})^2} = \frac{3520}{t_c+273} + \log p - 11{\cdot}349.$$

The numbers 2·073 and 4·146 are the densities referred to air of the molecules $C_2H_4O_2$ and $C_4H_8O_4$ respectively; D is the observed density; and 3520 and 11·349 are constants deduced from the determinations of Cahours and Bineau. This formula, of which the constants in its author's opinion can claim only approximate correctness, is quite inadequate to represent actual facts at high temperatures and high pressures where cohesion becomes marked. For example, it gives at a temperature of 280° for the density of the saturated vapour 35·13 instead of the observed number 62·62.

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* American Journal of Science and Arts, 1879, p. 277.

If our opinion be correct, and if the abnormal density of saturated vapours and of vapours near their saturation-points and also above their critical points, at high pressures, of stable substances, be due to mere molecular proximity, and not to any form of molecular combination; then a dissociating substance must exhibit a vapour-density which may be partly due to this cause. With such a substance as ammonium chloride, which, we have shown, is almost completely dissociated at 280°, the products of dissociation (hydrogen chloride and ammonia) are under such conditions of temperature and pressure that they would probably behave as perfect gases; the relatively few molecules of ammonium chloride which remain undecomposed in the gaseous state are under such low pressure, that their density is probably normal for the formula NH_4Cl; and in this case it is probable that the chemical factor alone determines the vapour-density. But with acetic acid the increase of density above 150° is evidently wholly due to the physical cause; while the abnormality is partly due to a physical, partly to a chemical, cause. It is, however, impossible in this case to ascertain at what temperature the physical cause begins to operate. It is evidently to be wished that, from a study of the behaviour of stable substances, some general law could be discovered which would embrace all instances of physical abnormality; and many attempts have been made in this direction, but as yet with only partial success. Willard Gibbs, on the other hand, has attacked the problem from the chemical side; and we have shown that his formula ceases to apply when the physical change becomes predominant.

Messrs. E. and L. Natanson* have recently published a research on the vapour-densities of nitric peroxide (N_2O_4 or NO_2), which, taken in conjunction with experiments of ours on the vapour-pressures of that body (Phil. Trans. 1886, Part I.), affords a striking confirmation of the correctness of our views. They give an isolated observation at −12°·6; and isothermals at 0°, 21°, 49°·7, 73°·7, 99°·8, 129°·9, and 151°·4. The limit of pressure was 800 millim. Now the boiling-point of nitric peroxide is, from our measurements, 21°·8; hence the densities of the saturated vapour are deducible from only the first three of the Messrs. Natansons' isothermals. We have plotted their results on curve-paper; this has shown us the regularity and trustworthiness of their observations; and by continuing the curves in the direction in which they run until they intersect the straight lines denoting vapour-pressures at the temperatures at which their measurements were made (using for this purpose the vapour-pressures determined by us), the density of the saturated vapour is determined with but small error.

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* Wiedemann's *Annalen*, 1886, p. 606.

The Natansons' numbers are as follows:—

Temp.	Pressure.	Density.	Temp.	Pressure.	Density.
	millim.	millim.		millim.	millim.
−12°·6	115·4	52·54	21°	491·60	38·74
0·0	37·96	35·84		516·96	39·01
	86·57	38·59		553·50	39·15
	172·48	40·71		639·17	39·64
	250·66	41·90			

At −12°·6 the vapour-pressure of nitric peroxide is 125 mm. The density of the saturated vapour must therefore be a little above 52·54. Now the theoretical density of N_2O_4 is 46. It may be that the higher density is due to experimental error; but from graphic representation of the Natansons' results this appears improbable. If the measurement is correct, it would imply that the chemical combination of molecules of NO_2 is not complete when the molecular complexity is represented by the formula $(NO_2)_2$, but may extend to $(NO_2)_3$, or even further. At 0° the vapour-pressure is 255 millim.; again the density found by the Natansons must be nearly that of saturation. At 21° the vapour-pressure is about 700 millim.; and a prolongation of the curve constructed from the above numbers would cut the line representing the large alteration of volume with no rise of vapour-pressure at a vapour-density of about 40. It is evident, then, that with nitric peroxide, as with acetic acid, the density of the saturated vapour rises with fall of pressure and temperature. Now it is known that nitric peroxide dissociates, for the physical properties (colour, &c.) change, on change of $(NO_2)^n$ into $n(NO_2)$; and the similarity of behaviour between nitric peroxide and acetic acid renders the dissociation of acetic acid from $(C_2H_4O_2)_n$ into $n(C_2H_4O_2)$ no longer conjectural.

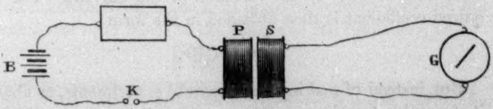
If it be granted that our thesis is proved, that the molecules of stable liquids are not more complex than those of their gases, it follows that the difference between liquids and gases is one of degree, not of kind; is quantitative, and not qualitative.

University College, Bristol,
November 18, 1886.

XXIII. *Note on a Method of Determining Coefficients of Mutual Induction. By* G. Carey Foster, *F.R.S.*[*]

The determination in absolute measure of the coefficient of mutual induction of two electric circuits by the ordinary method founded on the throw of a ballistic galvanometer is a somewhat complicated matter, necessarily occupying a good deal of time. But the process may be greatly simplified if we have available a condenser of which the capacity is accurately known. For instance, if P and S are two coils whose coefficient of mutual induction is required, let them first be joined up, as indicated in fig. 1—P in a primary circuit containing a battery, B, and make-and-break key, K; and S in a secondary circuit of total resistance r including a ballistic galvanometer G. Then, on closing or opening the key K, a momentary deflection of the galvanometer will occur in consequence of its being traversed by a quantity

Fig. 1.



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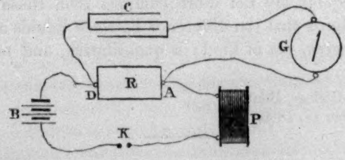
[*] Read November 27, 1886.

of electricity Q given by

$$Q = M\frac{\gamma}{r},$$

where M is the coefficient of mutual induction between P and S, and γ the strength of the primary current. Next, leaving the primary circuit unaltered, let connections be made as indicated by fig. 2, where C is a condenser of known capacity C, and A and D are two points in the primary circuit separated by a resistance R. Then, on making or breaking contact at K, the galvanometer is traversed by a quantity Q′, such that

Fig. 2.



$$Q' = \gamma CR.$$

If the points A and D are found by trial so that the deflection of the galvanometer is the same in both cases, we have

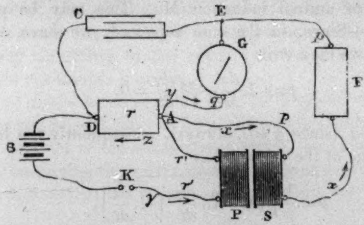
$$M = CRr.$$

This mode of working, however, has the obvious defect that the result, as stated, implies that the current in the battery-circuit is of exactly the same strength during each part of the experiment. As this cannot be looked for, it would be needful to include a measuring galvanometer in the battery-circuit, so as to take account of the variation of the current. The required coefficient is then obtained in the form

$$M = \frac{\gamma_2}{\gamma_1} CRr.$$

But, instead of making two separate experiments, as above, it is simpler to adopt an arrangement of apparatus which is very nearly a combination of the two arrangements just described. A single experiment then takes the place of two, and, instead of having to reproduce a particular deflection of the galvanometer, we have to adjust a resistance so as to prevent deflection. The connections will be understood by reference to fig. 3, where, so far as the reference-letters used in the previous figures recur, they have the meanings already given to them. The observation consists in adjusting a set of resistance-coils at F, between the galvanometer and the coil S, until there is no throw of the galvanometer on making or breaking contact at K.

Fig. 3.



Let the resistances ASFE, AGE, AD be represented by p, q, r respectively, and the corresponding currents by x, y, z. Further, let the current in the battery and primary coil be denoted by γ, the coefficient of self-induction of the coil S by L, and the potentials at the points A and E by A and E respectively.

When the battery-current has attained its steady value, it is evident that the currents x and y will both be nothing, and therefore that $A=E$, and that the charge of the condenser will be $C\gamma r$. But if there has been no throw of the galvanometer-needle, the average value of the current y during the whole time of establishment of the battery-current has been $=0$. Consequently, the total quantity conveyed by the current x has been equal to the charge of the condenser, or

$$\int_0^\infty x dt = C\gamma r.$$

But, if the average strength of the current $y=0$, the average difference of potentials $A-E=0$, and the effective electromotive force in the conductor p is that due to the mutual induction of the coils P and S (for the integral value of the electromotive force of self-induction must vanish). Hence

$$\int_0^\infty x\,dt = \frac{M}{p}\int_0^\infty \frac{d\gamma}{dt}\,dt = C\gamma r,$$

or

$$M = Cpr.$$

In order that the galvanometer-current y may be zero at every instant, as well as on the average, during the establishment of the primary current, it is essential that the coefficient of self-induction, L, of the coil S should be equal to the coefficient of mutual induction M. This may be proved as follows:—Since, in the case supposed, we have always $A-E=0$, we may write

$$px+L\frac{dx}{dt}-M\frac{d\gamma}{dt}=0.$$

But $x=\gamma-z$ (since $y=0$, always), consequently the instantaneous value of the current x is

$$x=\frac{1}{p}\left[(M-L)\frac{d\gamma}{dt}+L\frac{dz}{dt}\right],$$

and the simultaneous charge of the condenser is

$$Crz=\int_0^t xdt=\frac{1}{p}\left[(M-L)\gamma+Lz\right],$$

or

$$(M-L)\gamma=(Cpr-L)z.$$

But, since it has been already proved that $M=Cpr$ when the average current through the galvanometer vanishes, the last equation becomes

$$(M-L)\gamma=(M-L)z,$$

which requires either (1) that $\gamma=z$ (that is, that the primary current has become steady), or (2) that $M-L=0$.

When the last-mentioned condition is satisfied, we ought to be able to replace the galvanometer between the points A and E by a telephone, and to employ a rapid make-and-break *.

By using a pair of coils of known and invariable coefficient of mutual induction, the experimental process described above may afford a ready way of determining the capacity of a condenser; but for this purpose the method does not appear to possess any advantage over the well-known methods of De Sauty and Sir William Thomson for determining the capacity of condensers by comparison with a known standard,

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* Experiments in this direction, made since the reading of this paper before the Physical Society, by Mr. F. Womack, have not yet led to a fully satisfactory result.

more especially as a known condenser is more frequently at hand than a pair of coils of known coefficient *.

The limit of accuracy attainable in measurements by the method here described depends essentially upon the sensitiveness of the galvanometer employed; but with a given galvanometer, the method is susceptible of various degrees of accuracy according to the relative values given to the two variable resistances p and r.

These should be so adjusted that, for a given value of the difference $Cpr-M$, that is, for a given error in the adjustment of the product of the resistances p and r, the quantity of electricity traversing the galvanometer may be as great as possible. This requires that the resistances should fulfil the condition

$$\frac{p}{r}=\frac{q}{r'},$$

where r' is the resistance between A and D through the primary coil and battery. Let X and Y stand for the integrals $\int_0^\infty xdt$ and $\int_0^\infty ydt$ respectively, that is, for the total currents through the secondary coil and through the galvanometer. Then, equating the integral values of the electromotive force between A and E derived by considering the paths A G E and A F E, respectively, we get

$$pX-qY=M\frac{E}{r+r'},$$

E being here the electromotive force of the battery B.

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* Since this paper was read, Professor Ròiti, of Florence, has kindly sent me a copy of a paper communicated by him to the Royal Academy of Sciences of Turin (Memoirs of the Academy, series ii., vol. xxxviii.), in which he describes a method, very similar to that indicated in the text, for the absolute measurement of the capacity of condensers, using for the purpose a pair of coils whose coefficient of mutual induction is accurately known from their dimensions and relative positions. The chief difference between Professor Ròiti's arrangement and that given in this paper is that, instead of inserting the galvanometer between the points marked A and E in fig. 3, he includes it in the branch, A F E, containing the secondary coil. Between A and E he places a contact-key H, which, as well as the key K, is opened and closed mechanically, the two keys being moved by cranks attached to the same axle at right angles to each other.

Again, the final charge of the condenser is

$$X+Y=CE\frac{r}{r+r'}.$$

Eliminating X from these two equations,

$$\frac{Y}{Cpr-M}=\frac{E}{(r+r')(p+q)},$$

and this is to be as great as possible.

The denominator on the right may be written

$$pr\left(1+\frac{r'}{r}+\frac{q}{p}+\frac{qr'}{pr}\right);$$

the last term inside the bracket is the product of the second and third, and may be taken as constant, since q, the resistance of the galvanometer, and r', the resistance of the part of the circuit containing the primary coil, are practically determined by the apparatus employed, while pr has the constant value M/C. Hence, $Y/(Cpr—M)$ is greatest when $(p+q)(r+r')$ is least, or when $p/q=r/r'$, which is identical with the condition of maximum sensibility given above*.

In conclusion, I may give a few numerical results as examples of the applicability of the method; they are derived from experiments made in the laboratory of University College, London, by Mr. F. Womack, B.Sc.

A. *Small Induction-Coil* (without iron core). Approximate dimensions:—Primary: length 11·5 cm.; mean radius 2 cm.; wire, No. 20 B.W.G.; resistance 1·65 ohm. Secondary: length 10·4 cm.; radius, inside 2·55 cm., outside 3·83 cm.; wire, No. 30 B.W.G.; resistance 194 ohms. Battery, 2 Groves. Condenser, 4·926 microfarads (by direct measurement with ballistic galvanometer). The secondary coil could slide endways while remaining coaxal with the primary. The first measurements were made with the centres of the primary and secondary as nearly coincident as possible, so as to give a maximum coefficient of induction. The following are the results obtained:—

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* For the mathematical theory of the method, so far as it is given above, I am greatly indebted to my friend Dr. A. H. Fison.

Ohms.		
r.	p (=secondary coil+resistance-box).	Product pr (absolute units).
15	194+217	6165×10^{18}
14	+247	6174
13	+282	6188
12	+322	6192
11	+367	6171
10	+423	6170
9	+490	6156
8	+576	6160
7	+688	6174
6	+835	6174

$$\text{Mean value of } M/C \;=\; 6172{\cdot}4 \times 10^{18}$$

Hence $M = 4{\cdot}926 \times 10^{-15} \times 6172 \times 10^{18} = 3{\cdot}0403 \times 10^{7}$.

In these experiments the value of q/r' was about

$$135/(1{\cdot}65 + {\cdot}6) = 60.$$

Hence the greatest sensibility would be with $p = 60r$. This condition was nearly fulfilled with

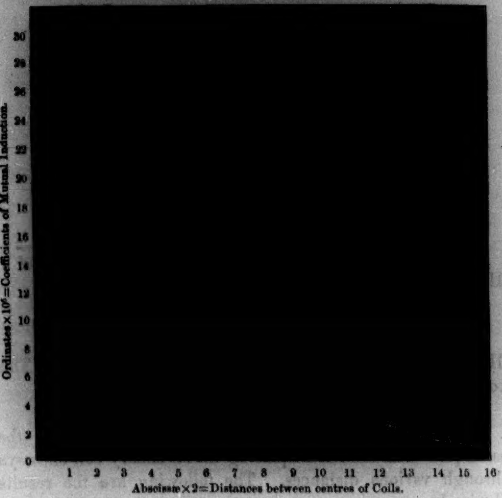
$$r = 10 \quad \text{and} \quad p = 194 + 423 = 617.$$

In the same way the values of M were obtained for the same pair of coils after displacing the secondary coil endways through various distances. The following are the results obtained :—

Distance between centres of coils. centim.	Value of M.
0·55	$304{\cdot}0 \times 10^{5}$
1·55	292·4
2·55	270·5
3·55	246·4
4·55	215·9
5·55	187·8
6·55	158·4
7·55	127·2
8·55	97·3
9·55	71·1
10·55	49·7
11·55	33·0
12·55	23·3
13·55	16·5
14·55	12·35
15·55	9·48

These values are represented graphically in the curve (fig. 4),

Fig. 4.



where ordinates denote values of M and abscissæ distances between the centres of the coils.

B. *Induction-Coil*, by Apps, capable of giving a 7-inch spark in air (presented to the University College Laboratory by Mr. J. Rose-Innes, B.Sc.). Length of secondary coil 21 cm., diameter (measured outside velvet covering) 11·3 cm. Resistance of primary wire = 0·278 ohm (at 16°·5); resistance of secondary wire 7394 ohms (at 16°·5). Battery, 1 Grove. $q = 135{\cdot}6$; $r' = 0{\cdot}58$ (about). Condenser, 4·926 microfarads.

Ohms.		pr
r.	p.	(absolute units).
27	7394 + 1550	$2{\cdot}415 \times 10^{23}$
28	+ 1250	2·420
29	+ 940	2·417
30	+ 650	2·413
31	+ 390	2·413
32	+ 150	2·414

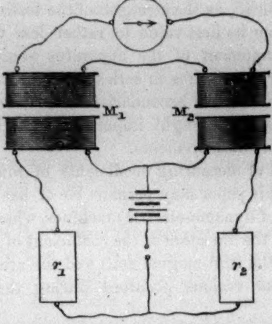
Mean value of M/C = $2{\cdot}415 \times 10^{23}$

Hence

$$M = 4{\cdot}926 \times 10^{-15} \times 2{\cdot}415 \times 10^{23}$$
$$= 1{\cdot}1896 \times 10^{9}.$$

As a further test of the accuracy of the method, the secondary wires of Apps's coil and of the small coil (A) were connected in circuit with each other and with a galvanometer, and the two primaries were connected so that the battery-current was divided between them, as shown in fig. 5. The connections being arranged so that the induced electromotive forces opposed each other, it was possible, by the proper adjustment of the resistances of the branches containing the two primary coils, to prevent the galvanometer being deflected when the battery-circuit was made or broken. When this adjustment is made, it is evident that the ratio of the resistances of the two primary circuits is the same as the ratio of the two coefficients of mutual induction. In this way, 39·45 was obtained as the ratio of the coefficients; whereas the condenser method described above gives $\frac{118{\cdot}96}{3{\cdot}0403} = 39{\cdot}13$, giving a difference of about 1 per cent. As, however, the current in the primary of the smaller coil has to be about forty times as strong as that in the large coil in the comparison experiments, in order that the induced electromotive forces may balance—and as,

Fig. 5.



moreover, the resistance of the copper wire of the former was a comparatively large fraction, at least one sixth or one seventh, of the whole resistance in circuit with it, while the copper resistance of the larger primary coil was not much more than one fifteen-hundredth of the whole resistance in circuit with it —the ratio of the resistances was no doubt somewhat disturbed by the unequal heating of the two primary circuits, and was in reality rather less than what was inferred from the marked values of the coils used. That this was the case was shown by the fact that the apparent ratio decreased progressively from 40·3 to 39·45, as the strength of the testing current was diminished from its first value to rather less than one sixth. A better arrangement of the apparatus would have been to put the two primary wires in series with the battery, and to have connected the two secondaries in parallel circuit; but the matter was not thought important enough to require a repetition of the measurements.

The method of measuring coefficients of mutual induction described in this paper may perhaps be of use in the experimental study of dynamo-electric machines, whose whole action depends upon the variation of the coefficient of mutual induction between the field-magnet coils and the armature coils, as the latter take various positions during the course of a revolution.

XXIV. *An Account of* Cauchy's *Theory of Reflection and Refraction of Light. By* JAMES WALKER, *M.A., Demonstrator at the Clarendon Laboratory, Oxford*[*].

THE theory of reflection and refraction of light holds such an important place among the problems of Optics which await their solution that it is advantageous to have a clear idea of the work which has been previously done in the subject.

The theory advanced by Green has been so thoroughly discussed by Lord Rayleigh and Sir W. Thomson that all questions connected with it may be considered as completely settled. But this is by no means the case with Cauchy's work on the subject; and some account of it may be of interest, even though the theory cannot be said to contribute much towards a solution of the problem.

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[*] Read December 11, 1886.

Several "reproductions"* of Cauchy's work have indeed appeared in French and German, but in most of them the elegance, and therewith the clearness, of Cauchy's method have been given up; while they leave in more or less obscurity the reasoning which led him to enunciate his "principle of continuity," and make no mention of a point of considerable interest, viz. the *mistake* which originally led to his adoption of a theory involving the strange assumption of a negative value for the coefficient of compressibility of the æther.

I.

Cauchy, at different periods, gave three distinct theories of reflection: the first two, however, require only a passing notice, as they were afterwards rejected by him as in no respect affording a complete solution of the problem.

The *first* theory was published in the *Bulletin de Férussac* of 1830. It rested on the true dynamical basis of the equality of pressures† at the interface of the media; but was vitiated by the neglect of the pressural waves, which must take part in the act of reflection and refraction. The method led, on the assumption of the equality of the density of the æther in the two media, to the formulæ given by Fresnel ‡.

The *second* theory was based on a method of obtaining the equations of condition at the interface, which was given in a lithographed memoir published in 1836. This method assumes a change in the equations of motion near the interface to a distance comparable with the radius of the sphere of activity of a molecule, and leads to the following theorem:—

"Etant donnés deux milieux ou deux systèmes de molécules separés l'un de l'autre par le plan de yz, supposons que des équations d'équilibre ou de mouvement généralisées de manière à subsister pour tous les points de l'un et de l'autre système et même pour les points situés sur la surface de séparation, l'on puisse déduire une équation de la forme

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* A. v. Ettingshausen, Pogg. *Ann.* l. p. 409; *Sitzb. der Wien. Akad.* xviii. p. 369. Beer, Pogg. *Ann.* xci. pp. 268, 467, 561; xcii. p. 402. Eisenlohr, Pogg. *Ann.* civ. p. 346. Briot, *Liouv. Journ.* (2nd) xi. p. 305; xii. p. 185. Lundquist, Pogg. *Ann.* clii. pp. 177, 308, 565.

† Cauchy's reasons for rejecting the principle of the equality of pressures at the interface are given in *Comptes Rendus*, xxviii. p. 60.

‡ Cauchy, *Mémoire sur la Dispersion*, § 10.

$$\frac{d^2 8}{dx^2} = \Theta,$$

8, Θ désignant deux quantités finies, mais variables avec les coordonnées $x\,y\,z$. On aura, pour $x=0$,

$$\frac{d8}{dx} = \frac{d8'}{dx}, \quad 8 = 8',$$

en admettant que l'on prenne pour premier et pour second membre de chacune des formules les resultâts que fournit la réduction de x à zéro, dans les deux valeurs de la fonction $\frac{d8}{dx}$ ou 8 relatives aux points intérieurs du premier et du second système."

The equations of condition resulting from the application of this theorem were published in Cauchy's memoir on Dispersion in the same year*. They express that the linear dilatation of the æther normal to the interface is the same for both the media, and that the rotations in the three coordinate planes of a particle at the interface is the same, whether the particle is considered as belonging to the first or second medium.

The method of deducing these conditions was given in a memoir presented to the French Academy on October 29, 1838†. This memoir has never been published; and all we know is that the method involved the assumption that the velocity of propagation of the pressural waves is very great compared with that of the distortional waves‡. In 1842 Cauchy showed that these conditions lead to Fresnel's formulæ§.

The *final* theory was published in detail‖ in the years 1838 and 1839, and is contained in the 8th and 9th volumes of the *Comptes Rendus*, and in the *Exercises d'Analyse et de Physique*. Later volumes of the *Comptes Rendus* contain re-statements of it; and in 1850 an extension of the method was made to rotatory isotropic media* and to anisotropic media†; but this later work was never completed.

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* *Mém. sur la Dispersion*, § 10.

† *Comptes Rendus*, vii. p. 751.

‡ *Ibid.* x. p. 905.

§ *Ibid.* xv. p. 418.

‖ The idea seems to be prevalent that we are indebted to the German reproductions for our knowledge of the details of Cauchy's method.

II.

Cauchy's final method‡ of determining the conditions at the interface of the media depended on finding the relations which must exist between the known values of the displacements in the interior of the medium, and the values, consistent with the conditions of the problem, which these displacements take when the change in the form of the equations of motion near the interface is taken into account.

Treating the æther as an isotropic elastic solid, for which the density is ρ, and the coefficients of compressibility and rigidity are k, n, the equations of motion are

$$\left.\begin{aligned}\rho\frac{d^2\xi}{dt^2}&=m\frac{d\delta}{dx}+n\nabla^2\xi,\\ \rho\frac{d^2\eta}{dt^2}&=m\frac{d\delta}{dy}+n\nabla^2\eta,\\ \rho\frac{d^2\zeta}{dt^2}&=m\frac{d\delta}{dz}+n\nabla^2\zeta,\end{aligned}\right\}\quad . \quad . \quad . \quad . \quad (1)$$

where

$$\delta=\frac{d\xi}{dx}+\frac{d\eta}{dy}+\frac{d\zeta}{dz},\quad \text{and } m=k+\tfrac{1}{3}n.$$

Sir W. Thomson§ has shown that all possible solutions of these equations are included in

$$\xi=\frac{d\phi}{dx}+u,\quad \eta=\frac{d\phi}{dy}+v,\quad \zeta=\frac{d\phi}{dz}+w,$$

where ϕ, u, v, w are some functions of x, y, z, t and u, v, w such that $\frac{du}{dx}+\frac{dv}{dy}+\frac{dw}{dz}=0$; further that, making these substitutions, equations (1) may be replaced by

$$\rho\frac{d^2\phi}{dt^2}=(m+n)\nabla^2\phi,\quad \rho\frac{d^2u}{dt^2}=n\nabla^2u,\quad \rho\frac{d^2v}{dt^2}=n\nabla^2v,$$
$$\rho\frac{d^2w}{dt^2}=n\nabla^2w.$$

So that there are two modes of waves possible: a condensational wave, propagated with velocity $\sqrt{\frac{m+n}{\rho}}$, and for which the velocity-potential is ϕ; and a distortional wave, propagated with the velocity $\sqrt{\frac{n}{\rho}}$, and for which the components of the displacement are u, v, w.

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* *C. R.* xxxi. pp. 160, 225.

† *Ibid.* xxxi. pp. 257, 297.

‡ *Ibid.* viii. pp. 374, 432, 459.

§ Baltimore Lectures, p. 32.

Let the interface of the media be the plane of yz, and suppose the first medium on the side of positive x.

Considering only plane waves, which have the same period of vibration $2\pi/\omega$ and the same trace $by+cz=0$ on the interface of the media, the values of ϕ, u, v, w satisfying the equations may be taken as

$$\begin{aligned}
\phi &= \frac{B_{\prime\prime}}{\sqrt{-1}}e^{(a_{\prime\prime}x+by+cz-\omega t)\sqrt{-1}} + \frac{C_{\prime\prime}}{\sqrt{-1}}e^{(-a_{\prime\prime}x+by+cz-\omega t)\sqrt{-1}}{}^{*},\\
u &= A\,e^{(ax+by+cz-\omega t)\sqrt{-1}} + A_{\prime}\,e^{(-ax+by+cz-\omega t)\sqrt{-1}},\\
v &= B\,e^{(ax+by+cz-\omega t)\sqrt{-1}} + B_{\prime}\,e^{(-ax+by+cz-\omega t)\sqrt{-1}},\\
w &= C\,e^{(ax+by+cz-\omega t)\sqrt{-1}} + C_{\prime}\,e^{(-ax+by+cz-\omega t)\sqrt{-1}};
\end{aligned}$$

where

$$a_{\prime\prime}=+\sqrt{\frac{\rho\omega^2}{m+n}-b^2-c^2},\quad a=+\sqrt{\frac{\rho\omega^2}{n}-b^2-c^2},$$

and A, B, C; $A_{\prime}$, $B_{\prime}$, $C_{\prime}$ are connected by the relations

$$Aa+Bb+Cc=0,\quad -A_{\prime}a+B_{\prime}b+C_{\prime}c=0.$$

The corresponding values of ξ, η, ζ are accordingly

$$\left.\begin{aligned}
\xi &= Ae^{(ax+by+cz-\omega t)\sqrt{-1}} + A_{\prime}e^{(-ax+by+cz-\omega t)\sqrt{-1}} + B_{\prime\prime}a_{\prime\prime}e^{(a_{\prime\prime}x+by+cz-\omega t)\sqrt{-1}}\\
&\qquad - C_{\prime\prime}a_{\prime\prime}e^{(-a_{\prime\prime}x+by+cz-\omega t)\sqrt{-1}},\\
\eta &= Be^{(ax+by+cz-\omega t)\sqrt{-1}} + B_{\prime}e^{(-ax+by+cz-\omega t)\sqrt{-1}} + B_{\prime\prime}be^{(a_{\prime\prime}x+by+cz-\omega t)\sqrt{-1}}\\
&\qquad + C_{\prime\prime}be^{(-a_{\prime\prime}x+by+cz-\omega t)\sqrt{-1}},\\
\zeta &= Ce^{(ax+by+cz-\omega t)\sqrt{-1}} + C_{\prime}e^{(-ax+by+cz-\omega t)\sqrt{-1}} + B_{\prime\prime}ce^{(a_{\prime\prime}x+by+cz-\omega t)\sqrt{-1}}\\
&\qquad + B_{\prime\prime}ce^{(-a_{\prime\prime}x+by+cz-\omega t)\sqrt{-1}}.
\end{aligned}\right\}\quad(2)$$

Now within the medium the displacements are those due to the distortional waves alone, and hence the values of ξ, η, ζ are

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[*] The $\sqrt{-1}$ is inserted for convenience.

$$\left.\begin{aligned}\xi&=\mathrm{A}e^{(ax+by+cz-\omega t)\sqrt{-1}}+\mathrm{A}_{,}e^{(-ax+by+cz-\omega t)\sqrt{-1}},\\ \eta&=\mathrm{B}e^{(ax+by+cz-\omega t)\sqrt{-1}}+\mathrm{B}_{,}e^{(-ax+by+cz-\omega t)\sqrt{-1}},\\ \zeta&=\mathrm{C}e^{(ax+by+cz-\omega t)\sqrt{-1}}+\mathrm{C}_{,}e^{(-ax+by+cz-\omega t)\sqrt{-1}};\end{aligned}\right\}\quad . \quad (3)$$

whence, comparing these values with equations (2),

$$\mathrm{B}_{,,}=\mathrm{C}_{,,}=0^{*}.$$

Near the interface, and for values of x less than the small quantity ϵ, the differential equations change form by the addition of terms whose coefficients are functions of x, which vanish when x exceeds the small quantity ϵ. These additional terms may be reduced to linear functions of ξ, η, ζ, and their differential coefficients with respect to x[†], since the equations will still be satisfied by taking the displacements proportional to the same exponential $e^{(by+cz-\omega t)\sqrt{-1}}$.

We require now to determine the values of ξ, η, ζ which satisfy these altered equations.

Cauchy's method of doing this depends, as v. Ettingshausen[‡] has pointed out, on the method of the variation of parameters: by this method the constants A, $\mathrm{A}_{,}$... are treated as functions of x; and a first condition imposed upon them is that $\frac{d\xi}{dx}$, $\frac{d\eta}{dx}$, $\frac{d\zeta}{dx}$ must remain unaltered in form, so that

$$\left.\begin{aligned}\frac{d\xi}{dx}&=\Big\{\mathrm{A}ae^{(ax+by+cz-\omega t)\sqrt{-1}}-\mathrm{A}_{,}ae^{(-ax+by+cz-\omega t)\sqrt{-1}}\\ &\qquad+\mathrm{B}_{,,}a_{,,}^{2}e^{(a_{,,}x+by+cz-\omega t)\sqrt{-1}}+\mathrm{C}_{,,}a_{,,}^{2}e^{(-a_{,,}x+by+cz-\omega t)\sqrt{-1}}\Big\}\sqrt{-1},\\ \frac{d\eta}{dx}&=\Big\{\mathrm{B}ae^{(ax+by+cz-\omega t)\sqrt{-1}}-\mathrm{B}_{,}ae^{(-ax+by+cz-\omega t)\sqrt{-1}}\\ &\qquad+\mathrm{B}_{,,}a_{,,}be^{(a_{,,}x+by+cz-\omega t)\sqrt{-1}}-\mathrm{C}_{,,}a_{,,}be^{(-a_{,,}x+by+cz-\omega t)\sqrt{-1}}\Big\}\sqrt{-1},\\ \frac{d\zeta}{dx}&=\Big\{\mathrm{C}ae^{(ax+by+cz-\omega t)\sqrt{-1}}-\mathrm{C}_{,}ae^{(-ax+by+cz-\omega t)\sqrt{-1}}\\ &\qquad+\mathrm{B}_{,,}a_{,,}ce^{(a_{,,}x+by+cz-\omega t)\sqrt{-1}}-\mathrm{C}_{,,}a_{,,}ce^{(-a_{,,}x+by+cz-\omega t)\sqrt{-1}}\Big\}\sqrt{-1}.\end{aligned}\right\}\ (4)$$

Consider now any one of the parameters, say $\mathrm{B}_{,,}$; its value deduced from equations (2) and (4) is of the form

$$\mathrm{B}_{,,}=\left(\lambda\xi+\mu\eta+\nu\zeta+\pi\frac{d\xi}{dx}+\rho\frac{d\eta}{dx}+\sigma\frac{d\zeta}{dx}\right)e^{-(a_{,,}x+by+cz-\omega t)\sqrt{-1}}.$$

Differentiating this equation with respect to x, and substitu-

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[*] *C. R.* viii. p. 440.

[†] *Tom. cit.* p. 461.

[‡] Pogg. *Ann.* l. p. 409.

ting for $\frac{d^2\xi}{dx^2}, \frac{d^2\eta}{dx^2}, \frac{d^2\zeta}{dx^2}$ from the changed differential equations, all the terms will cancel out except those which depend on the change of form; and we shall have

$$\frac{dB_{\prime\prime}}{dx}=\left(L\xi+M\eta+N\zeta+P\frac{d\xi}{dx}+R\frac{d\eta}{dx}+S\frac{d\zeta}{dx}\right)e^{-(a_{\prime\prime}x+by+cz-\omega t)\sqrt{-}}$$

where L, M, ... vanish for finite values of x.

Now the values of ξ, η, ζ will differ but slightly from those given by (3), so that this last expression may be written

$$\frac{dB_{\prime\prime}}{dx}=(AL+BM+\ldots)e^{(a-a_{\prime\prime})x\sqrt{-1}}+(A_{\prime}L+B_{\prime}M+\ldots)e^{-(a+a_{\prime\prime})x\sqrt{-1}},$$

whence the variable part of $B_{\prime\prime}$ is

$$B_{\prime\prime}=\int(AL+BM+\ldots)e^{(a-a_{\prime\prime})x\sqrt{-1}}dx$$
$$+\int(A_{\prime}L+B_{\prime}M+\ldots)e^{-(a+a_{\prime\prime})x\sqrt{-1}}dx.$$

Similar values are obtained for the parts of A, $A_{\prime}$, ... which depend on x. Now L, M, ... vanish for finite values of x; so that if $\int_0^x L\,dx, \int_0^x M\,dx$, ... are very small relatively to $\lambda, \mu, \nu, \ldots$[*], the variable part of $B_{\prime\prime}$ may be neglected if $-(a+a_{\prime\prime})\sqrt{-1}$, $(a-a_{\prime\prime})\sqrt{-1}$ have no real positive part; so that those among the coefficients A, $A_{\prime}$, ... will remain unaltered, when the change in the medium near the interface is taken into account, which have the coefficient of x in their exponential factor with a real part *not less than* that of $a\sqrt{-1}$.

In the present case this will be so for all the parameters except $B_{\prime\prime}$; and hence, calling $\bar{\xi}$, $\bar{\eta}$, $\bar{\zeta}$ the corrected values of ξ, η, ζ, we have

$$\bar{\xi}=Ae^{(ax+by+cz-\omega t)\sqrt{-1}}+A_{\prime}e^{(-ax+by+cz-\omega t)\sqrt{-1}}+B_{\prime\prime}a_{\prime\prime}e^{(a_{\prime\prime}x+by+cz-\omega t)\sqrt{-1}},$$
$$\bar{\eta}=Be^{(ax+by+cz-\omega t)\sqrt{-1}}+B_{\prime}e^{(-ax+by+cz-\omega t)\sqrt{-1}}+B_{\prime\prime}be^{(a_{\prime\prime}x+by+cz-\omega t)\sqrt{-1}},$$
$$\bar{\zeta}=Ce^{(ax+by+cz-\omega t)\sqrt{-1}}+C_{\prime}e^{(-ax+by+cz-\omega t)\sqrt{-1}}+B_{\prime\prime}ce^{(a_{\prime\prime}x+by+cz-\omega t)\sqrt{-1}},$$

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[*] This necessitates, first, that the coefficients of the added terms in the altered differential equations are all finite, and their product by ϵ very small; secondly, that the thickness of the modified layer is small compared with the wave-length (*Comptes Rendus*, viii. p. 439; ix. p. 5).

$$\frac{d\bar{\xi}}{dx} = \Big\{\mathrm{A}ae^{(ax+by+cz-\omega t)\sqrt{-1}} - \mathrm{A}_{\prime}ae^{(-ax+by+cz-\omega t\sqrt{-1}}$$
$$+\mathrm{B}_{\prime\prime}a_{\prime\prime}{}^{2}e^{(a_{\prime\prime}x+by+cz-\omega t)\sqrt{-1}}\Big\}\sqrt{-1},$$

$$\frac{d\bar{\eta}}{dx} = \Big\{\mathrm{B}ae^{(ax+by+cz-\omega t)\sqrt{-1}} - \mathrm{B}_{\prime}ae^{(-ax+by+cz-\omega t)\sqrt{-1}}$$
$$+\mathrm{B}_{\prime\prime}a_{\prime\prime}be^{(a_{\prime\prime}x+by+cz-\omega t)\sqrt{-1}}\Big\}\sqrt{-1},$$

$$\frac{d\bar{\zeta}}{dx} = \Big\{\mathrm{C}ae^{(ax+by+cz-\omega t)\sqrt{-1}} - \mathrm{C}_{\prime}ae^{(-ax+by+cz-\omega t)\sqrt{-1}}$$
$$+\mathrm{B}_{\prime\prime}a_{\prime\prime}ce^{(a_{\prime\prime}x+by+cz-\omega t)\sqrt{-1}}\Big\}\sqrt{-1};$$

or, if

$\left.\begin{array}{l}\xi,\ \eta,\ \zeta\\ \xi_{\prime},\ \eta_{\prime},\ \zeta_{\prime}\\ \xi_{\prime\prime},\ \eta_{\prime\prime},\ \zeta_{\prime\prime}\end{array}\right\}$ are the components of the displacements in the $\left\{\begin{array}{l}\text{incident}\\ \text{reflected}\\ \text{pressural}\end{array}\right\}$ wave, $\bar{\xi}$, $\bar{\eta}$, $\bar{\zeta}$ are such that

$$\bar{\xi}=\xi+\xi_{\prime}+\xi_{\prime\prime},\quad \bar{\eta}=\eta+\eta_{\prime}+\eta_{\prime\prime},\quad \bar{\zeta}=\zeta+\zeta_{\prime}+\zeta_{\prime\prime};$$
$$\frac{d\bar{\xi}}{dx}=\frac{d\xi}{dx}+\frac{d\xi_{\prime}}{dx}+\frac{d\xi_{\prime\prime}}{dx},\quad \frac{d\bar{\eta}}{dx}=\frac{d\eta}{dx}+\frac{d\eta_{\prime}}{dx}+\frac{d\eta_{\prime\prime}}{dx},\quad \frac{d\bar{\zeta}}{dx}=\frac{d\zeta}{dx}+\frac{d\zeta_{\prime}}{dx}+\frac{d\zeta_{\prime\prime}}{dx}.$$

In the same way, for the second medium the corrected values of the displacements are such that

$$\bar{\xi}'=\xi'+\xi'',\qquad \bar{\eta}'=\eta'+\eta'',\qquad \bar{\zeta}'=\zeta'+\zeta'';$$
$$\frac{d\bar{\xi}'}{dx}=\frac{d\xi'}{dx}+\frac{d\xi''}{dx},\quad \frac{d\bar{\eta}'}{dx}=\frac{d\eta'}{dx}+\frac{d\eta''}{dx},\quad \frac{d\bar{\zeta}'}{dx}=\frac{d\zeta'}{dx}+\frac{d\zeta''}{dx},$$

where

$\left.\begin{array}{l}\xi',\ \eta',\ \zeta'\\ \xi'',\ \eta'',\ \zeta''\end{array}\right\}$ are the components of the displacements in the $\left\{\begin{array}{l}\text{refracted}\\ \text{pressural}\end{array}\right\}$ wave.

Finally, *assuming**, that for $x=0$,

$$\bar{\xi}=\bar{\xi}',\ \bar{\eta}=\bar{\eta}',\ \bar{\zeta}=\bar{\zeta}',\quad \frac{d\bar{\xi}}{dx}=\frac{d\bar{\xi}'}{dx},\quad \frac{d\bar{\eta}}{dx}=\frac{d\bar{\eta}'}{dx},\quad \frac{d\bar{\zeta}}{dx}=\frac{d\bar{\zeta}'}{dx},\tag{5}$$

we have as the interfacial conditions, that for $x=0$,

$$\left.\begin{array}{ll}\xi+\xi_{\prime}+\xi_{\prime\prime}=\xi'+\xi'', & \eta+\eta_{\prime}+\eta_{\prime\prime}=\eta'+\eta'',\\ & \zeta+\zeta_{\prime}+\zeta_{\prime\prime}=\zeta'+\zeta'',\\ \dfrac{d\xi}{dx}+\dfrac{d\xi_{\prime}}{dx}+\dfrac{d\xi_{\prime\prime}}{dx}=\dfrac{d\xi'}{dx}+\dfrac{d\xi''}{dx}, & \dfrac{d\eta}{dx}+\dfrac{d\eta_{\prime}}{dx}+\dfrac{d\eta_{\prime\prime}}{dx}=\dfrac{d\eta'}{dx}+\dfrac{d\eta''}{dx},\\ & \dfrac{d\zeta}{dx}+\dfrac{d\zeta_{\prime}}{dx}+\dfrac{d\zeta_{\prime\prime}}{dx}=\dfrac{d\zeta'}{dx}+\dfrac{d\zeta''}{dx}.\end{array}\right\}(6)$$

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* *C. R.* ix. p. 94.

These equations express Cauchy's principle of the continuity of the motion of the æther, according to which the incident wave passes into the reflected and refracted waves "sans transition brusque."

Judging from the historical sequence of Cauchy's papers, there can be little doubt that he enunciated this principle as the physical interpretation of the result arrived at by reasoning analogous to the above; it is, however, impossible to agree with v. Ettingshausen that "Cauchy hat diese Gleichungen (6) anfänglich aus Gründen gerechtfertigt, die sich auf das Verfahren der Variationen der Constanten zurückführen lassen;"[*] as the principle is already involved in the assumption (5)[†].

All that the above analysis really leads to, and all that Cauchy[‡] claimed to have established by it, is the necessity for including the pressural waves in the problem of reflection and refraction.

Since the true dynamical equations of condition, given by the equality of displacements and pressures, are that for $x=0$,

$$\left.\begin{array}{c}\bar{\xi}=\bar{\xi}', \qquad \bar{\eta}=\bar{\eta}', \qquad \bar{\zeta}=\bar{\zeta}', \\ (m-n)\bar{\delta}+2n\dfrac{d\bar{\xi}}{dx}=(m'-n')\bar{\delta}'+2n'\dfrac{d\bar{\xi}'}{dx}, \\ n\left(\dfrac{d\bar{\xi}}{dy}+\dfrac{d\bar{\eta}}{dx}\right)=n'\left(\dfrac{d\bar{\xi}'}{dy}+\dfrac{d\bar{\eta}'}{dx}\right), \quad n\left(\dfrac{d\bar{\zeta}}{dx}+\dfrac{d\bar{\xi}}{dz}\right)=n'\left(\dfrac{d\bar{\zeta}'}{dx}+\dfrac{d\bar{\xi}'}{dz}\right),\end{array}\right\}(7)$$

it is clear, as has been often pointed out, that Cauchy's assumption involves that of the identity of the statical properties of the æther in the two media. Lundquist[§], however, considers that "Cauchy has established his principle of continuity by the aid of analysis, the exactitude of which it is not easy to contest;" and hence that this result, combined with the dynamically exact conditions (7), proves "the legitimacy of Green's assumption of the equality of the compressibility and the rigidity of the æther in the two media."

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[*] *Sitzb. der Wien. Akad.* xviii. p. 371.

[†] I do not think Cauchy contemplated a continuous rapid transition of one medium into the other (*cf. C. R.* x. p. 347); neither does v. Ettingshausen in his paper. Supposing the assumption justified on these grounds, yet, as von der Mühl has pointed out, the former assumption respecting the coefficients of the additional terms in the modified equations precludes the assumption of a finite change in the statical properties of the media (*Matt. Ann.* v. p. 477).

[‡] *C. R.* x. p. 347.

[§] Pogg. *Ann.* clii. p. 185.

Cauchy himself did not see that this was involved in his conditions; and so in what follows the compressibilities and rigidities of the two media will be considered as unequal.

III.*

Taking, as before, the interface of the media as the plane of yz, and the first medium on the side of positive x, let the axis of z be parallel to the plane of the waves, so that the plane of xy is the plane of incidence; then, if $\xi\ \eta\ \zeta$ and $\xi'\ \eta'\ \zeta'$ denote the components of the displacements in the first and second medium respectively, $\xi\ \eta\ \zeta$, $\xi'\ \eta'\ \zeta'$ will be independent of z.

(1) Let the incident vibrations be perpendicular to the plane of incidence.

The general equations of motion are in this case

$$\rho\frac{d^2\zeta}{dt^2}=n\left(\frac{d^2\zeta}{dx^2}+\frac{d^2\zeta}{dy^2}\right),\quad \rho'\frac{d^2\zeta'}{dt^2}=n'\left(\frac{d^2\zeta'}{dx^2}+\frac{d^2\zeta'}{dy^2}\right),$$

and the principle of continuity gives for the interfacial conditions that for $x=0$,

$$\zeta=\zeta',\qquad \frac{d\zeta}{dx}=\frac{d\zeta'}{dx}.$$

Assuming

$$\zeta=\mathrm{C}e^{(ax+by-\omega t)\sqrt{-1}}+\mathrm{C}_{,}e^{(-ax+by-\omega t)\sqrt{-1}},$$

$$\zeta'=\quad e^{(a'x+by-\omega t)\sqrt{-1}};$$

we get at once

$$\mathrm{C}=\frac{a+a'}{2a},\qquad \mathrm{C}_{,}=\frac{a-a'}{2a},$$

$$\therefore\ \mathrm{C}_{,}=\frac{a-a'}{a+a'}=-\frac{\sin(i-r)}{\sin(i+r)},$$

since

$$\frac{b}{a}=\tan i,\quad \frac{b}{a'}=\tan r;$$

where i, r are the angles of incidence and refraction.

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[*] *C. R.* viii. p. 985; ix. pp. 1, 59, 91, 676, 726, 727; x. p. 347. *Ex. d'An. et de Phys.* i. pp. 133, 212.

(2) Let the incident vibrations be in the plane of incidence. The equations of motion in the first medium are

$$\left\{\begin{aligned}\rho\frac{d^2\xi}{dt^2}&=m\frac{d}{dx}\left(\frac{d\xi}{dx}+\frac{d\eta}{dy}\right)+n\left(\frac{d^2\xi}{dx^2}+\frac{d^2\xi}{dy^2}\right),\\ \rho\frac{d^2\eta}{dt^2}&=m\frac{d}{dy}\left(\frac{d\xi}{dx}+\frac{d\eta}{dy}\right)+n\left(\frac{d^2\eta}{dx^2}+\frac{d^2\eta}{dy^2}\right).\end{aligned}\right.$$

Using Green's* method of separating the distortional and condensational parts of the solution, and assuming

$$\xi=\frac{d\phi}{dx}+\frac{d\psi}{dy},\quad \eta=\frac{d\phi}{dy}-\frac{d\psi}{dx},$$

the equations of motion become

$$\frac{d^2\phi}{dt^2}=g^2\left(\frac{d^2\phi}{dx^2}+\frac{d^2\phi}{dy^2}\right),\quad \frac{d^2\psi}{dt^2}=\gamma^2\left(\frac{d^2\psi}{dx^2}+\frac{d^2\psi}{dy^2}\right),$$

where

$$g^2=(m+n)/\rho,\quad \gamma^2=n/\rho.$$

Similar equations apply to the second medium.

The principle of continuity gives for the interfacial conditions that for $x=0$,

$$\left.\begin{aligned}\frac{d\phi}{dx}+\frac{d\psi}{dy}&=\frac{d\phi'}{dx}+\frac{d\psi'}{dy}\\ \frac{d\phi}{dy}-\frac{d\psi}{dx}&=\frac{d\phi'}{dy}-\frac{d\psi'}{dx}.\end{aligned}\right\}\quad .\ .\ .\ .\ \ (8)$$

$$\left.\begin{aligned}\frac{d^2\phi}{dx^2}+\frac{d^2\psi}{dxdy}&=\frac{d^2\phi'}{dx^2}+\frac{d^2\psi'}{dxdy}\\ \frac{d^2\phi}{dxdy}-\frac{d^2\psi}{dx^2}&=\frac{d^2\phi'}{dxdy}-\frac{d^2\psi'}{dx^2}\end{aligned}\right\}\quad .\ .\ .\ \ (9)$$

Since these equations are true for all values of y, we may differentiate with respect to it, and hence, by means of the equations of motion, replace (9) by

$$\frac{1}{g^2}\frac{d^2\phi}{dt^2}=\frac{1}{g'^2}\frac{d^2\phi'}{dt^2},\quad \frac{1}{\gamma^2}\frac{d^2\psi}{dt^2}=\frac{1}{\gamma'^2}\frac{d^2\psi'}{dt^2}\ .\ .\ .\ .\ \ (9a)$$

It may here be noted, that if we take the general equations of condition (7) and assume the equality of the rigidities of the æther in the two media with no assumption respecting the compressibilities, we get, instead of (9a),

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* Collected Works, p. 261.

$$\rho\frac{d^2\phi}{dt^2}=\rho'\frac{d^2\phi'}{dt^2},\quad \rho\frac{d^2\psi}{dt^2}=\rho'\frac{d^2\psi'}{dt^2}\quad . \quad . \quad . \quad . \qquad (9b)$$

Assume

$$\begin{aligned}\phi &= \mathrm{B}_{,,}e^{(a_{,,}x+by-\omega t)\sqrt{-1}},\\ \psi &= \mathrm{A}e^{(ax+by-\omega t)\sqrt{-1}}+\mathrm{A}_{,}e^{(-ax+by-\omega t)\sqrt{-1}},\\ \phi' &= \mathrm{B}''e^{(a''x+by-\omega t)\sqrt{-1}},\\ \psi' &= e^{(a'x+by-\omega t)\sqrt{-1}}.\end{aligned}$$

The equations of motion give

$$\omega^2=\gamma^2(a^2+b^2)=g^2(a_{,,}{}^2+b^2)=\gamma'^2(a'^2+b^2)=g'^2(a''^2+b^2);$$

whence

$$a_{,,}=\ \ b\sqrt{1-\frac{\omega^2}{g^2b^2}}\cdot\sqrt{-1}=\ \ bu_{,,}\sqrt{-1},\text{ say};$$

$$a''=-b\sqrt{1-\frac{\omega^2}{g'^2b^2}}\cdot\sqrt{-1}=-bu''\sqrt{-1},\text{ say},$$

the negative sign being taken, as the second medium corresponds to negative x.

From equations (8) and (9a) we get

$$\left.\begin{aligned}u_{,,}\mathrm{B}_{,,}\sqrt{-1}+(\mathrm{A}+\mathrm{A}_{,})&=-u''\mathrm{B}''\sqrt{-1}+1,\\ b\mathrm{B}_{,,}-a(\mathrm{A}-\mathrm{A}_{,})&=b\mathrm{B}''-a',\\ \frac{1}{g^2}\mathrm{B}_{,,}&=\frac{1}{g'^2}\mathrm{B}'',\\ \frac{1}{\gamma^2}(\mathrm{A}+\mathrm{A}_{,})&=\frac{1}{\gamma'^2}.\end{aligned}\right\}\quad . \qquad (10)$$

The last two of these equations give

$$\mathrm{A}+\mathrm{A}_{,}=\frac{\gamma^2}{\gamma'^2}=\mu^2,$$

where μ is the refractive index, and

$$\mathrm{B}_{,,}=\frac{g^2}{g'^2}\mathrm{B}''=\frac{a''^2+b^2}{a_{,,}{}^2+b^2}\mathrm{B}''=\mu_0{}^2\mathrm{B}'',\text{ say}.$$

Substituting in the first two of equations (10), we get

$$(u_{,,}\mathrm{B}_{,,}+u''\mathrm{B}'')\sqrt{-1}=1-\mu^2,$$

whence

$$\mathrm{B}'' = \frac{\mu^2-1}{\mu_0{}^2 u_{,,} + u''}\sqrt{-1},$$

and

$$\mathrm{A}-\mathrm{A}_{,} = \frac{a'}{a} + \frac{b}{a}(\mathrm{B}_{,,}-\mathrm{B}'')$$

$$= \frac{a'}{a} + \frac{b}{a}(\mu^2-1)\mathrm{M}\sqrt{-1},$$

where

$$\mathrm{M} = \frac{\mu_0{}^2-1}{\mu_0{}^2 u_{,,} + u''}.$$

Hence

$$2\mathrm{A} = \mu^2 + \frac{a'}{a} + \frac{b}{a}(\mu^2-1)\mathrm{M}\sqrt{-1}$$

$$= \frac{a'^2+b^2}{a^2+b^2} + \frac{a'}{a} + \frac{b}{a}\cdot\frac{a'^2-a^2}{a^2+b^2}.\mathrm{M}\sqrt{-1}$$

$$= \frac{(aa'+b^2)+b(a'-a)\mathrm{M}\sqrt{-1}}{a(a^2+b^2)}(a'+a) = 2\mathrm{R}e^{\delta\sqrt{-1}}, \text{ say};$$

$$2\mathrm{A}_{,} = \frac{(aa'-b^2)-b(a'+a)\mathrm{M}\sqrt{-1}}{a(a^2+b^2)}.(a'-a) = 2\mathrm{R}_{,}e^{\delta_{,}\sqrt{-1}}, \text{ say}.$$

Then R, R, denote the amplitudes of the incident and reflected vibrations, and δ, δ, the difference of phase between the incident and refracted, the reflected and refracted waves respectively.

Hence, if α is the azimuth with respect to the plane of incidence of the incident vibration, the reflected vibration will in general be elliptical with a difference of phase $\delta_{,}-\delta$ between the components in and perpendicular to the plane of incidence; and if this difference of phase is destroyed, the azimuth β of the resulting rectilinear vibration will be given by

$$\cot\beta = \mathrm{R}_{,}/\mathrm{C}_{,}.$$

Hence

$$\frac{\cot\beta}{\cot\alpha}e^{(\delta_{,}-\delta)\sqrt{-1}} = -\frac{(aa'-b^2)-b(a'+a)\mathrm{M}\sqrt{-1}}{(aa'+b^2)+b(a'-a)\mathrm{M}\sqrt{-1}}; \quad . \quad (11)$$

and

$$\frac{\cot^2\beta}{\cot^2\alpha} = \frac{(aa'-b^2)^2+b^2(a'+a)^2\mathrm{M}^2}{(aa'+b^2)^2+b^2(a'-a)^2\mathrm{M}^2}$$

$$= \frac{\cos^2(i+r)+\mathrm{M}^2\sin^2(i+r)}{\cos^2(i-r)+\mathrm{M}^2\sin^2(i-r)};$$

also

$$\tan(\delta_{,}-\delta)=\frac{\mathrm{M}\{\tan(i+r)+\tan(i-r)\}}{1-\mathrm{M}^2\tan(i+r)\tan(i-r)}.$$

*Total Reflection**.

If μ is less than unity, we may write $\mu=\sin \mathrm{I}$, and we get

$$a'^2=\frac{4\pi^2}{\lambda'^2}\cos^2 r=\frac{4\pi^2}{\lambda^2}\sin(\mathrm{I}-i)\sin(\mathrm{I}+i).$$

Hence, if $i>\mathrm{I}$, the value of a' becomes imaginary, and the refracted ray will die out as it leaves the refracting surface.

Writing

$$\mathrm{U}=\sin^{\frac{1}{2}}(i-\mathrm{I})\sin(i+\mathrm{I}),$$

we must substitute in the formulæ obtained above

$$a'=-\frac{2\pi}{\lambda}\mathrm{U}\cdot\sqrt{-1},$$

the negative sign being taken, as the second medium is on the side of negative x.

Substituting this value, we find that the reflection is total both for the vibration in the plane of incidence, and for the vibration perpendicular to the plane of incidence, and for the difference of phase between the components of the reflected ray we get from (11)

$$\frac{\cot\beta}{\cot\alpha}\cdot e^{(\delta_{,}-\delta)\sqrt{-1}}=\frac{\sin i(\sin i+\mathrm{UM})+\cos i(\mathrm{M}\sin i+\mathrm{U})\sqrt{-1}}{\sin i(\sin i+\mathrm{UM})-\cos i(\mathrm{M}\sin i+\mathrm{U})\sqrt{-1}};$$

whence

$$\tan\frac{\delta_{,}-\delta}{2}=\frac{\cos i\{\mathrm{M}\sin i+\sin^{\frac{1}{2}}(i-\mathrm{I})\sin^{\frac{1}{2}}(i+\mathrm{I})\}}{\sin i\{\sin i+\mathrm{M}\sin^{\frac{1}{2}}(i-\mathrm{I})\sin^{\frac{1}{2}}(i+\mathrm{I})\}}$$

$$=\frac{\mathrm{M}\dfrac{\sin^2\mathrm{I}}{\sin i}+\sin^{\frac{1}{2}}(i-\mathrm{I})\sin^{\frac{1}{2}}(i+\mathrm{I})}{\sin^2 i}\cdot\cos i,$$

if the square and higher powers of the small quantity M are neglected.

Cauchy has $\sin^2 i$ instead of $\sin^2 \mathrm{I}$ in the numerator of the last expression; the correct formula was first given by Beer[*].

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* *C. R.* ix. p. 764; xxx. p. 465.

IV.[†]

Before proceeding further, it will be as well to discuss the value of the expression denoted above by M.

Cauchy, not seeing that his equations of condition involved the assumption of the identity of the statical properties of the æther in the two media, adopted the following relations,

$$m+n=-\epsilon^2 n, \quad m'+n'=-\epsilon'^2 n';$$

where ϵ, ϵ' are very small numerics.

These relations give

$$\mu_0{}^2=\frac{m+n}{\rho}\times\frac{\rho'}{m'+n'}=\mu^2\frac{\epsilon^2}{\epsilon'^2},$$

$$u_{\prime\prime}=\sqrt{1-\frac{n}{(m+n)\sin^2 i}}=\sqrt{1+\frac{1}{\epsilon^2\sin^2 i}}\bumpeq\frac{1}{\epsilon\sin i},$$

$$u''=\bumpeq\frac{1}{\epsilon'\sin r}.$$

Hence

$$\mathrm{M}=\frac{\mu^2\frac{\epsilon^2}{\epsilon'^2}-1}{\mu^2\frac{\epsilon^2}{\epsilon'^2}\cdot\frac{1}{\epsilon\sin i}+\frac{1}{\epsilon'\sin r}}=\epsilon\sin i-\epsilon'\sin r=\mathrm{E}\sin i,$$

if $\mathrm{E}=\epsilon-\frac{\epsilon'}{\mu}$[‡].

No attempt has been made, so far as I am aware, to indicate the reasons which led to Cauchy's adoption of the above remarkable relations between the coefficients of compressibility and rigidity of the æther in a medium.

In order to find a relation between the coefficients, Cauchy considered the condition which must be fulfilled if the incident light is completely polarized by reflection.

This condition is that $\mathrm{M}=0$, giving since

$$\mathrm{M}=\frac{\mu_0{}^2-1}{\mu_0{}^2 u_{\prime\prime}+u''}=\frac{u_{\prime\prime}-u''}{1-u_{\prime\prime}u''},$$

where $u_{\prime\prime}$, u'' are both positive, that

$$u_{\prime\prime}=u'', \text{ or } \frac{\rho}{m+n}=\frac{\rho'}{m'+n'}.$$

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[*] Pogg. *Ann.* xci. p. 274. [†] *C. R.* ix. pp. 691, 727.

[‡] *C. R.* xxviii. p. 64. Originally Cauchy took $\epsilon=0$.

In his first memoir on the subject, Cauchy*, forgetting to take into account the fact of the media being on different sides of the plane of yz, wrote

$$a''=bu''\sqrt{-1},$$

where u'' is positive.

Hence he obtained

$$\mathrm{M}=\frac{\mu_0^2-1}{\mu_0^2u_{\prime\prime}-u''}=\frac{u_{\prime\prime}+u''}{1+u_{\prime\prime}u''},$$

where $u_{\prime\prime}$, u'' are both positive, giving as the condition for complete polarization

$$u_{\prime\prime}=u''=\infty\,,\ \text{or}\ m+n=0=m'+n'.$$

He then argued that incomplete polarization must be due to the fact that these expressions differ slightly from zero, and that their value must be negative, in order that the pressural waves should be insensible at a distance from the interface for all angles of incidence.

In a memoir published in 1840 and in the *Exercises d'Analyse et de Physique*†, this mistake was corrected, and the true condition $\rho/(m+n)=\rho'/(m'+n')$ was given; but, apparently led astray by his original mistake and by a desire‡ (afterwards given up, *Compt. Rend.* xxviii. p. 125) to make complete polarization depend on the properties of the refracting medium alone, and not on any relation between the two media, he still adopted the solution

$$m+n=0=m'+n';$$

though he mentioned§ also the true solution, viz. that the coefficient of compressibility of the æther is infinite, and the wave-lengths of the pressural waves in the two media are equal.

Assuming that the æther is incompressible, the polarization of the reflected ray will be elliptical when the wave-lengths of the pressural waves are unequal, and we get

$$\mathrm{M}=\left(\frac{\lambda_{\prime\prime}^2}{\lambda''^2}-1\right)\Big/\left(\frac{\lambda_{\prime\prime}^2}{\lambda''^2}+1\right),$$

where $\lambda_{\prime\prime}$, λ'' are the wave-lengths of the pressural waves in the two media. This is Eisenlohr's suggestion; but the form in which he made it does not show that it involves the absolute incompressibility of the æther. If $\lambda_{\prime\prime}/\lambda''=\lambda/\lambda'$, we get Green's formula. Eisenlohr[*] says that this assumption is absolutely untenable: it is, however, as Green shows, a direct consequence of the assumption made by him, and involved in Cauchy's conditions, viz. the identity of the statical properties of the æther in the two media.

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* *C. R.* ix. p. 94. *Ex. d'An. et de Phys.* i. p. 167.

† *C. R.* x. p. 357. *Ex. d'An. et de Phys.* i. p. 233.

‡ *C. R.* ix. p. 727.

§ *Ibid.* x. p. 358.

Further than that, if we assume only the equality of the rigidities, the equations of condition become (8), (9*b*); whence

$$\frac{B_{\prime\prime}}{B''}=\frac{\rho'}{\rho}=\mu^2;$$

and if the æther is incompressible,

$$M=\frac{\mu^2-1}{\mu^2+1}.$$

Haughton's[†] suggestion that the coefficient of compressibility is very great, but not infinite, does not help matters; so that it would appear that the only way to escape the difficulty is by one of Lord Rayleigh's[‡] suggestions:—

(1) That "although the transition between the two media is so sudden that the principal waves of transverse vibrations are affected nearly in the same way as if it were instantaneous, yet we may readily imagine that the case is different for the surface-waves, whose existence is almost confined to the layer of variable density."

(2) That "the densities concerned in the propagation of the so-called longitudinal waves are unknown, and may possibly not be the same as those on which transverse vibrations depend."

Eisenlohr[§] gives another (it appears entirely empirical) value for M: it involves, as Cauchy's, a negative value for the coefficient compressibility of the æther, and leads to formulæ closely agreeing with experiment; as, however, they contain a third disposable constant, this close agreement is hardly to be wondered at.

V.

Cauchy's formulæ for metallic reflection were originally published on April 15, 1839[‖], and thus were obtained from his second set of equations of condition, in which the pressural waves were neglected. The formulæ were republished on January 17, 1848*, and apparently no attempt was made to obtain equations in which the influence of the pressural waves was included.

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[*] Pogg. *Ann.* civ. p. 358.

[†] Phil. Mag. [4] iv. p. 81.

[‡] *Ibid.* xlii. pp. 96, 97.

[§] Pogg. *Ann.* civ. p. 356.

[‖] *C. R.* viii. p. 553.

Cauchy considers the peculiarities of metallic reflection to be due to a complex value of the refractive index.

Writing

$$\mu=\theta e^{\epsilon\sqrt{-1}},$$

we get

$$a'^2=\frac{4\pi^2}{\lambda^2}\left(\theta^2 e^{2\epsilon\sqrt{-1}}-\sin^2 i\right)=\frac{4\pi^2}{\lambda^2}\,.\,\mathrm{U}^2 e^{2u\sqrt{-1}},\text{ say};$$

whence

$$\mathrm{U}^2\sin 2u=\theta^2\sin 2\epsilon,\quad \cot\overline{2u-\epsilon}=\cot\epsilon\cos\left(2\tan^{-1}\frac{\sin i}{\theta}\right).\tag{12}$$

Substituting

$$a'=-\frac{2\pi}{\lambda}\mathrm{U}e^{u\sqrt{-1}},\quad a=\frac{2\pi}{\lambda}\cos i,\quad b=\frac{2\pi}{\lambda}\sin i,$$

in the values of $\mathrm{C}_{/\!/}/\mathrm{C}$, $\mathrm{A}_{/\!/}/\mathrm{A}$, and making $\mathrm{M}=0$, we get at once Cauchy's well-known formulæ.

Making these same substitutions in (11), we get

$$\frac{\cot\beta}{\cot\alpha}e^{\Delta\sqrt{-1}}=\frac{\sin^2 i+\cos i\,\mathrm{U}e^{u\sqrt{-1}}}{\sin^2 i-\cos i\,\mathrm{U}e^{u\sqrt{-1}}};$$

whence

$$\tan\Delta=\frac{2\mathrm{U}\sin u\cos i\sin^2 i}{\sin^4 i-\mathrm{U}^2\cos^2 i}=\sin u\tan\left(2\tan^{-1}\frac{\mathrm{U}\cos i}{\sin^2 i}\right),$$

$$\frac{\cot^2\beta}{\cot^2\alpha}=\frac{\sin^4 i+\cos^2 i\,\mathrm{U}^2-2\sin^2 i\cos i\,\mathrm{U}\cos u}{\sin^4 i+\cos^2 i\,\mathrm{U}^2+2\sin^2 i\cos i\,\mathrm{U}\cos u},$$

$$=\cot(\psi-45^\circ),$$

where

$$\cot\psi=\cos u\sin\left(2\tan^{-1}\frac{\mathrm{U}\cos i}{\sin^2 i}\right),$$

or, if $\alpha=45^\circ$,

$$\cot 2\beta=\cos u\left(\sin 2\tan^{-1}\frac{\mathrm{U}\cos i}{\sin^2 i}\right).$$

At the polarizing angle I, for which $\Delta=\pi/2$, we have

$$\mathrm{U}=\tan\mathrm{I}\sin\mathrm{I},\quad u=2\beta,$$

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* *C. R.* xxvi. p. 86.

where β is the azimuth of the reflected vibrations, when the incident vibrations are in an azimuth 45° with respect to the plane of incidence.

These values substituted in equations (12) give the values of the constants θ, ϵ, and then these same equations serve for the determination of u, U for any other angle of incidence.

While the above equations can at the best be only considered incomplete, objections have also been made to the complex value of the refractive index involved in them.

Lord Rayleigh's criticism[*] that the real part of μ^2 should be positive, while the results of experiment substituted in Cauchy's equations give a value of μ^2 with its real part negative, seems not so much an argument against Cauchy's idea, as an "argument against the attempt to account for the effects on a purely elastic solid theory" [†].

The value of μ^2 resulting from Sir W. Thomson's theory of light is a real negative quantity; this value substituted in Green's equations gives the reflection total at all angles of incidence. For this result there is no experimental evidence at present, except in the case of silver. The same will result from Lord Rayleigh's extension of Green's theory, unless, as seems scarcely probable, the refractive index of the pressural waves is a complex quantity.

VI.

In August 1850[‡] Cauchy published the outlines of the result of applying his method to the case of reflection at the surface of an isotropic medium which possesses rotatory power.

The displacements in the upper medium are taken as

$$\xi = \mathrm{A}be^{(ax+by-\omega t)\sqrt{-1}} + \mathrm{A}_{,}be^{(-ax+by-\omega t)\sqrt{-1}} + \mathrm{B}_{,,}a_{,,}e^{(a_{,,}x+by-\omega t)\sqrt{-1}},$$

$$\eta = -\mathrm{A}ae^{(ax+by-\omega t)\sqrt{-1}} + \mathrm{A}_{,}ae^{(-ax+by-\omega t)\sqrt{-1}} + \mathrm{B}_{,,}be^{(a_{,,}x+by-\omega t)\sqrt{-1}},$$

$$\zeta = \frac{2\pi}{\lambda}\mathrm{C}e^{(ax+by-\omega t)\sqrt{-1}} + \frac{2\pi}{\lambda}\mathrm{C}_{,}e^{(-ax+by-\omega t)\sqrt{-1}};$$

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[*] Phil. Mag. [4] xliii. p. 325.

[†] Eisenlohr, Wied. *Ann.* i. p. 204; Glazebrook, Brit. Assoc. Report, 1885, p. 197.

[‡] *C. R.* xxxi. pp. 160, 225.

and those in the lower medium, since there will be two refracted waves circularly polarized in opposite directions,

$$\xi' = A_1' b e^{(a_1'x+by-\omega t)\sqrt{-1}} + A_2' b e^{(a_2'x+by-\omega t)\sqrt{-1}} + B'' a'' e^{(a''x+by-\omega t)\sqrt{-1}},$$

$$\eta' = -A_1' a_1' e^{(a_1'x+by-\omega t)\sqrt{-1}} - A_2' a_2' e^{(a_2'x+by-\omega t)\sqrt{-1}} + B'' b e^{(a''x+by-\omega t)\sqrt{-1}},$$

$$\zeta' = -\sqrt{-1}\,.\,A_1' \frac{2\pi}{\lambda_1'} e^{(a_1'x+by-\omega t)\sqrt{-1}} + \sqrt{-1}\,A_2' \frac{2\pi}{\lambda_2'} e^{(a_2'x+by-\omega t)\sqrt{-1}}.$$

Substituting these values in the equations of condition resulting from the principle of continuity, we get

$$\left.\begin{aligned} b(A+A_{,}-A_1'-A_2') &= B''a''-B_{\prime\prime}a'',\\ -(A-A_{,})a+A_1'a_1'+A_2'a_2' &= b(B''-B_{\prime\prime}),\\ b\{(A-A_{,})a-A_1'a_1'-A_2'a_2'\} &= (B''a''^2-B_{\prime\prime}a_{\prime\prime}^2),\\ -(A+A_{,})a^2+A_1'a_1'^2+A_2a_2'^2 &= b(B''a''-B_{\prime\prime}a''),\\ C+C_{,} &= \left(-\frac{\lambda}{\lambda_1'}A_1'+\frac{\lambda}{\lambda_2'}A_2'\right)\sqrt{-1},\\ (C-C_{,})a &= \left(-\frac{\lambda}{\lambda_1'}a_1'A_1'+\frac{\lambda}{\lambda_2'}a_2'A_2'\right)\sqrt{-1}. \end{aligned}\right\} \quad (13)$$

The last two of these equations give

$$\left.\begin{aligned} 2aC &= \left\{(a+a_2')\frac{\lambda}{\lambda_2'}A_2'-(a+a_1')\frac{\lambda}{\lambda_1'}A_1'\right\}\sqrt{-1},\\ 2aC_{,} &= \left\{(a-a_2')\frac{\lambda}{\lambda_2'}A_2'-(a-a_1')\frac{\lambda}{\lambda_1'}A_1'\right\}\sqrt{-1}. \end{aligned}\right\}. \quad (14)$$

From the first and fourth we get

$$A+A_{,} = \frac{\lambda^2}{\lambda_1'^2}A_1' + \frac{\lambda^2}{\lambda_2'^2}A_2', \quad . \quad . \quad . \quad . \quad (15)$$

and from the second and third

$$B_{\prime\prime} = \frac{a''^2+b^2}{a_{\prime\prime}^2+b^2}B'' = \mu_0^2 B'';$$

whence, writing as before,

$$\frac{\mu_0^2-1}{\mu_0^2 a_{\prime\prime}-a''}b = -M\sqrt{-1},$$

where M is the coefficient of ellipticity, and eliminating $B_{\prime\prime}$ B'' between the first two of equations (13),

$$(a-Mb\sqrt{-1})A-(a+Mb\sqrt{-1})A_{,} = (a_1'-Mb\sqrt{-1})A_1' + (a_2'-Mb\sqrt{-1})A_2',$$

and from (15)

$$2a\mathrm{A}=\mathrm{U}_1\mathrm{A}_1'+\mathrm{U}_2\mathrm{A}_2',\quad 2a\mathrm{A}_{,}=\mathrm{V}_1\mathrm{A}_1'+\mathrm{V}_2\mathrm{A}_2',\quad . \qquad (16)$$

where

$$\mathrm{U}_1=\{(aa_1'+b^2)+\mathrm{M}b(a_1'-a)\sqrt{-1}\}\frac{a_1'+a}{a^2+b^2}$$

$$=\frac{2\pi}{\lambda_1'}\{\cos(i-r_1)+\mathrm{M}\sin(i-r_1)\sqrt{-1}\}\frac{\sin(i+r_1)}{\sin r_1},$$

$$\mathrm{V}_1=\{(aa_1'-b^2)-\mathrm{M}b(a_1'+a)\sqrt{-1}\}\frac{a_1'-a}{a^2+b^2}$$

$$=\frac{2\pi}{\lambda_1'}\{\cos(i+r_1)-\mathrm{M}\sin(i+r_1)\sqrt{-1}\}\frac{\sin(i-r_1)}{\sin r_1},$$

and $\mathrm{U}_2\,\mathrm{V}_2$ are similar expressions with $(_2)$ written instead of $(_1)$.

First, consider the case in which the incident vibrations are perpendicular to the plane of incidence.

Then $\mathrm{A}=0$, and equation (15) and the first of equations (16) give

$$\mathrm{A}_{,}=\frac{\lambda^2}{\lambda_1'^2}\mathrm{A}_1'+\frac{\lambda^2}{\lambda_2'^2}\mathrm{A}_2',\quad \mathrm{U}_1\mathrm{A}_1'+\mathrm{U}_2\mathrm{A}_2'=0,$$

whence from (14)

$$\frac{\mathrm{A}_{,}}{\frac{\lambda^2}{\lambda_1'^2}\mathrm{U}_2-\frac{\lambda^2}{\lambda_2'^2}\mathrm{U}_1}=\frac{2a\sqrt{-1}\mathrm{C}}{\frac{\lambda}{\lambda_2'}(a+a_2')\mathrm{U}_1+\frac{\lambda}{\lambda_1'}(a+a_1')\mathrm{U}_2}$$

$$=\frac{2a\sqrt{-1}\,\mathrm{C}_{,}}{\frac{\lambda}{\lambda_2'}(a-a_2')\mathrm{U}_1+\frac{\lambda}{\lambda_1'}(a-a_1')\mathrm{U}_2},$$

and writing for U_1, U_2, a, a_1', a_2', b their values in terms of the angles of incidence and refraction,

$$\mathrm{A}_{,}=-\sqrt{-1}\;\frac{\sin 2i\sin\frac{r_1-r_2}{2}\cdot[\cos 2\mathrm{R}-\mathrm{M}\sin 2\mathrm{R}\sqrt{-1}]}{\mathrm{D}\left[\sin^2(i+\mathrm{R})-\sin^2\frac{r_1-r_2}{2}\right]}.\mathrm{C},$$

$$\mathrm{C}_{,}=-\frac{\mathrm{D}\sin(i-\mathrm{R})\sin(i+\mathrm{R})+\mathrm{D}'\sin^2\frac{r_1-r_2}{2}}{\mathrm{D}\left[\sin^2(i+\mathrm{R})-\sin^2\frac{r_1-r_2}{2}\right]}.\mathrm{C};$$

where

$$D = \cos(i-R) + M \sin(i-R)\sqrt{-1},$$

$$D' = \cos(i+R) - M \sin(i+R)\sqrt{-1},$$

$$R = \frac{r_1+r_2}{2}, \text{ the mean angle of refraction.}$$

Omitting squares and products of the small quantities M, $\sin\frac{r_1-r_2}{2}$, the formulæ become

$$A_{,} = -\sqrt{-1}\,\frac{\sin 2i \sin\frac{r_1-r_2}{2} \,.\, \cos 2R}{[\cos(i-R)+M\sin(i-R)\sqrt{-1}]\sin^2(i+R)}\,C,$$

$$C_{,} = -\frac{\sin(i-R)}{\sin(i+R)}\,C.$$

Hence the reflected ray will be in general elliptically polarized, except for an angle of incidence such that the angle of mean refraction is $\pi/4$, in which case the reflected ray will be plane-polarized with vibrations perpendicular to the plane of incidence. In all cases the component perpendicular to the plane of incidence is practically the same as if the medium had no rotating power, the other component being very small.

Next consider the case in which the incident vibrations are in the plane of incidence.

Then $C=0$, and from equation (14)

$$A_1' = \frac{\lambda_1'}{\lambda_2'} \cdot \frac{a+a_2'}{a+a_1'} \,.\, A_2',$$

and hence

$$\frac{C_{,}}{(a_1'-a_2')} = \frac{\frac{\lambda^2}{\lambda_1'\lambda_2'}\,aA_{,}\sqrt{-1}}{\frac{\lambda}{\lambda_2'}(a+a_2')V_1 + \frac{\lambda}{\lambda_1'}(a+a_1')V_2}$$

$$= \frac{\frac{\lambda^2}{\lambda_1'\lambda_2'}\,aA\sqrt{-1}}{\frac{\lambda}{\lambda_2'}(a+a_2')U_1 + \frac{\lambda}{\lambda_1'}(a+a_1')U_2}.$$

Whence

$$C_{,} = \sqrt{-1}\,.\,\frac{\sin 2i \sin\frac{r_1-r_2}{2}}{D\left[\sin^2(i+R) - \sin^2\frac{r_1-r_2}{2}\right]}\,.\,A,$$

$$A_{,} = \frac{D'\sin(i+R)\sin(i-R) + D\sin^2\frac{r_1-r_2}{2}}{D\left[\sin^2(i+R) - \sin^2\frac{r_1-r_2}{2}\right]}\,.\,A\,;$$

or, to the same degree of approximation as in the former case,

$$C_{,} = \sqrt{-1}\sin 2i\,\frac{\sin\frac{r_1-r_2}{2}}{\left[\cos(i-R) + M\sin(i-R)\sqrt{-1}\right]\sin^2(i+R)}\,.\,A,$$

$$A_{,} = \frac{\cos(i+R) - M\sin(i+R)\sqrt{-1}}{\cos(i-R) + M\sin(i-R)\sqrt{-1}}\,.\,\frac{\sin(i-R)}{\sin(i+R)}\,.\,A.$$

Hence the reflected ray will be in general elliptically polarized, the component of the vibration in the plane of incidence being practically the same as if the refracting medium had no rotating power, the component of the vibration perpendicular to the plane of incidence being extremely small. At the polarizing angle for which $R+i=\pi/2$, the reflected vibration is plane-polarized, and the vibrations will be at an azimuth with respect to the plane of incidence given by

$$\tan\beta = \tan 2i\,.\,\frac{\sin\frac{r_1-r_2}{2}}{M}.$$

VII.

In the same year (1850) Cauchy extended his method to the problem of crystalline reflection: the complete solution was given in a memoir presented to the French Academy on September 16, 1850*.

This memoir was never published, though it was announced† to appear in the 23rd volume of the *Mémoires de l'Académie*; and we have only slight indications of Cauchy's manner of dealing with the problem.

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* *C. R.* xxxi. p. 422.

† *Tom. cit.* p. 509.

In accordance with the results of his theory of double refraction, Cauchy does not suppose the vibrations to be necessarily strictly transversal and longitudinal[*]. In order to eliminate the amplitudes of the latter vibrations, he assumes as an approximation the strict transversality of the former, and thus obtains[†] four equations between the quasi-transversal amplitudes, which contain three coefficients, whose values are known when coordinate axes are taken depending on the refracting surface and the plane of incidence.

A second memoir[‡] is devoted to the determination of the value of these coefficients, when fixed directions in the crystal are taken as the axes. The value of this determination is lessened by the fact, that at the very commencement an approximation is made depending on the peculiar relation between the coefficients of elasticity, which we have considered above.

This is all that has been published, except some notes indicating a few of the results of his analysis; it is, however, *probable*[§] that Cauchy first obtained a solution on the assumption of the strict transversality of the luminous vibrations, and then proceeded to apply corrections to the values thus obtained, and it is *possible*[‖] that he adopted in the solution MacCullagh's idea of uniradial directions.

There is no need to enter further into this part of Cauchy's work, as Briot[¶] has employed both these methods in his excellent adaptation of Cauchy's theory to the problem of Crystalline Reflection.

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[*] *C. R.* xxxi. pp. 258, 299.

[†] *Tom. cit.* p. 257.

[‡] *Tom. cit.* p. 297.

[§] *Tom. cit.* p. 160.

[‖] *Tom. cit.* p. 532.

[¶] *Liouv. Journ.* [2] xii. p. 185

PROCEEDINGS

OF

THE PHYSICAL SOCIETY

OF LONDON.

April 1887.

XXV. *The Permanent and Temporary Effects on some of the Physical Properties of Iron, produced by raising the Temperature to 100° C.* *By* Herbert Tomlinson, *B.A.* *

Introduction.

For many years I have been carrying on researches respecting the effects of stress on the physical properties of matter, and during this period I have become acquainted with certain phenomena, which, though pertaining more or less to most metals, are so conspicuous in iron as to render it worthy of special attention. As these phenomena bear importantly on what Sir William Thomson has designated the thermodynamic qualities of metals, the investigation of which seems to be attracting daily more and more attention, I propose to lay before the Physical Society, from time to time, such information concerning them as a patient study has enabled me to acquire.

On the present occasion I would invite attention to certain remarkable effects produced on some of the physical properties of iron, by merely raising the temperature to a degree not exceeding 100° C.

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* Read January 22, 1887.

The Internal Friction of Iron.

If an iron wire be suspended vertically with its upper extremity clamped to a rigid support, and its lower one clamped or soldered to the centre of a horizontal bar of metal, attached to which, at equal distances from the wire, are two cylinders of equal mass and dimensions, and the whole system be set in torsional oscillation, the amplitude of the vibrations will be found to diminish more or less gradually until finally rest ensues. This diminution of amplitude is almost entirely due to two causes, namely, the friction of the air, and the internal friction of the metal. The internal friction of the wire may be measured by the logarithmic decrement of arc for a single vibration, or by $\frac{\log A - \log B}{n}$, where A is the initial arc, and B is the arc after n vibrations. By the aid of Prof. G. G. Stokes's mathematical formulæ [*], and an experimental determination by myself [†] of the coefficient of viscosity of air, I have been able to eliminate the resistance of the air, and to compute the damping effect due to the internal friction of the metal. Where the deformations produced are sufficiently small, I have proved the following laws respecting the logarithmic decrement of arc [‡]:—

1. It is independent of the amplitude;
2. It is independent of the vibration-period.

These laws only hold good when the wire has been allowed to rest for a considerable time after any change has been made in the arrangements, and when there has been a large number of oscillations executed previously to the actual testing.

What is the nature of this so-called internal friction of the metal? It cannot resemble fluid friction; because for such velocities as we have here the friction of fluids is proportional to the velocity. Neither can it resemble altogether the external friction of solids; because the latter is not nearly so independent of the velocity as is the internal friction, nor would the logarithmic decrement be independent of the amplitude. Some experiments by Prof. G. Wiedemann* throw light on the subject. Let $A_0 B_0$ represent the original position of equilibrium of the axis of the bar to which the wire is attached, and let a torsional couple be applied so as to bring the bar to $A_1 B_1$. On reducing the torsional stress gradually to zero the bar will not come back to $A_0 B_0$, but remain in a new position $A_2 B_2$, however small may have been the angle of torsion $A_1 0 A_0$. Again, if the bar be twisted by an equal torsional stress in the opposite direction to $A_3 B_3$ and the stress be then reduced to zero, the bar will remain permanently twisted in the position $A_4 B_4$. Now if we keep on applying and removing the torsional couple in this way, first in one direction and then in the other, the region $A_2 0 A_4$ will gradually diminish until a minimum is reached. According to Wiedemann, this is exactly what takes place when we allow the wire to vibrate freely; the permanent position of equilibrium is constantly shifted to and fro. Within the regions $A_1 0 A_2$ and $A_3 0 A_4$ the elasticity is perfect, and there is on the whole no gain or loss of energy. The loss of energy experienced in a torsionally vibrating wire arises from the work expended in the region $A_2 0 A_4$ in shifting the permanent position of equilibrium from A_2 to A_4 and back again; and, provided the amplitudes of the oscillations do not exceed a certain limit, the extent of the region $A_2 0 A_4$ is proportional to the amplitude. Wiedemann goes further than this; for he says what is true with respect to the wire as a whole is true

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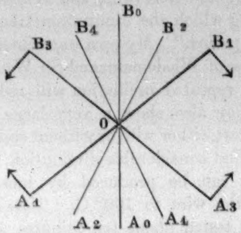
[*] Camb. Phil. Soc. Trans. vol. ix. no. x. (1850).

[†] Phil. Trans. 1886.

[‡] "The Internal Friction of Metals," Phil. Trans. 1886.



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* Wiedemann's *Annalen*, 1879, No. 4, vol. vi.; Phil. Mag. January and February 1880.

with respect to each molecule of the iron, and that the internal friction is really due to the rotation to and fro of the permanent positions of equilibrium of the molecules. We need not stop to discuss here this last point; but what does seem probable is, that the main part of the loss of energy is experienced as the bar swings from A_2 to A_4. When, as in my own experiments, the deformations produced by the oscillations are very small, it would seem that the positions A_2, A_4 are really subpermanent rather than permanent; and if time were given and the molecules agitated, the bar would of itself return to the position A_0, when the torsional couple was reduced to zero.

I have said, that as the wire oscillates, the region $A_2\,0\,A_4$ becomes narrower and narrower, and Wiedemann speaks of the period during which the diminution takes place, as "the accommodation period." My own experiments have verified the results of those of Wiedemann and Sir William Thomson *, in showing that repeated oscillation will reduce the internal friction; but they also show a very large influence to be exerted by long rest, either with or without oscillation, and have further proved that considerable diminution, both temporary and permanent, can be produced by merely raising the temperature of the wire to 100° C. Thus a well annealed iron wire, when tested about ten minutes after suspension, was found to have a logarithmic decrement due to the internal friction of the metal of ·003011, after one hour of ·001195, and after one day of ·001078. After the last period the friction became sensibly constant, and after four days was found to be still the same; the wire had apparently "accommodated" itself as far as possible.

Great, however, as was the reduction of the internal friction produced by oscillation and rest, the minimum had by no means been reached; for on repeatedly heating the wire to 100° C. and then allowing it to cool, the logarithmic decrement rapidly diminished, until after six days, on each of which the wire was heated to 100°C., and then allowed to cool slowly, it became only ·000412, when further repetition of the above process ceased to sensibly affect the friction. The greater part of the diminution occurred after the first heating and cooling, but several repetitions were necessary to produce the minimum mentioned above.

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* Proc. Roy. Soc. May 18, 1865.

Still more marvellous is the temporary effect of a rise of temperature not exceeding 100° C. on the internal friction of annealed iron. A careful examination of the above specimen at temperatures ranging between 0° C. and 100° C. revealed the astonishing fact that, at a temperature of 98° C., the logarithmic decrement was only ·000112, and was considerably less than one fourth of its amount at 0° C.* At 98° C. the friction was a minimum, further rise of temperature resulting in increase of the logarithmic decrement. It may perhaps assist us in forming some notion of the very small amount of internal friction in the above specimen of iron at 98° C., if we estimate the number of vibrations which would be required before the amplitude would be reduced to one half of its initial value by molecular friction only: this number is nearly 3000. It follows that if we could make the wire and its appendages vibrate *in vacuo*, and maintain the temperature constantly at 98° C., with a vibration-period of ten seconds, more than eight hours would elapse before an initial amplitude of 100 would be reduced to 50.

The internal friction of the wire when reduced to its minimum by all the above-mentioned processes was only *one thirtieth* of its original amount.

When the wire has fully "accommodated" itself, a very small cause will disturb the accommodation: a mechanical shock, a change of load, a slight rise or fall of temperature, or even rotation of the molecules by magnetic stress, will necessitate fresh oscillations before the friction again reaches its minimum. Consequently, if a wire be raised to 100° C., and be then cooled again rather quickly, it does not immediately regain the accommodation which it had before heating. The time taken by the wire to reaccommodate itself when the accommodation has been disturbed by change of temperature, depends considerably upon the direction of the change. Thus, when the wire is raised from the temperature of the room to 100° C., the reaccommodation is effected in a very much shorter time than when the accommodation has been disturbed by lowering the temperature from 100° C. to the temperature of the room.

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* The temporary diminution of the internal friction of annealed iron was shown at the meeting of the Society.

I am inclined to regard both the temporary and permanent alterations of the internal friction of iron, which are produced by rise of temperature not exceeding 100° C., to be partly due to mere agitation of the molecules, but the permanent effects do not seem to be entirely due to molecular agitation ; for the maintaining of the temperature at 100° C. for some time does not bring down the friction anything like so much as repeated heating and cooling. It would seem that the slow shifting backwards and forwards of the molecules induced by the last process is in a great measure to be credited with the permanent diminution of friction, in the same manner that the shifting backwards and forwards of the molecules caused by torsional oscillation has been shown to produce permanent diminution.

The Longitudinal and Torsional Elasticity of Iron.

It might readily be imagined that since the internal friction of iron is so considerably altered by change of temperature, the elasticity would be correspondingly affected. This, however, is not so ; both the torsional and longitudinal elasticity of iron are affected by raising the temperature to 100° C., but not nearly to the same extent as the internal friction. Thus an annealed iron wire, when suspended ready for torsional vibration, was heated slightly by passing the flame of a Bunsen's burner rather quickly up and down it several times. The time of vibration before heating was 1·154 second ; and in 5 minutes, 35 minutes, and 245 minutes after cooling was 1·147, 1·142, and 1·136 second respectively. Here we have a small, though distinct, permanent increase of elasticity ; and it will be noticed that time is an important element in the amount of increase. Again, by a very carefully conducted set of observations, I have shown that the torsional elasticity of annealed iron is temporarily *decreased* to the extent of 2·693 per cent., when the temperature is raised from 0° to 100° C.*

Again, an annealed pianoforte-steel wire, when tested with a certain load at the temperature of 12° C., was temporarily elongated to the extent of 1·502 half-millimetres; when heated to 100° C. in an air-chamber the elongation was 1·487 half-millimetres; and when cooled again and tested 24 hours afterwards, was elongated by 1·450 half-millimetres [*]. Thus, as with the torsional elasticity, there was a permanent increase of elasticity, and a *temporary decrease* of 2·58 per cent. Time in this case also is an important element, for the elasticity immediately after cooling was very appreciably less than when a long rest had been given.

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* Proc. R. S. No. 244, 1886.

Similarly, I have shown both for longitudinal and torsional elasticity that an iron wire, after having been permanently extended by traction, has its elasticity very perceptibly increased by long rest. It is also well known that the portative power of a magnet can be considerably increased by putting on the load by small quantities at a time, with long intervals of rest between.

These and other considerations prove beyond a doubt, that if the molecular arrangement of iron be disturbed by any kind of stress whatever, exceeding a certain small limit, the molecules will not assume at ordinary temperatures those positions which will secure a maximum of elasticity, until a rest of many hours has been given.

The Velocity of Sound in Iron.

According to Wertheim, the velocity of sound in iron and steel is increased by a rise of temperature not extending beyond 100° C.[†] Now in no sense whatever is this statement correct. It is true that the longitudinal elasticity of iron, as determined by the method of statical extension, may be found greater at 100° C. than at 0° C., provided we begin with the lower temperature first and the wire has not been previously tested at 100° C. But, as we have seen, the apparent *temporary* increase of elasticity is really a *permanent* one; and if the wire be repeatedly heated to 100° C. and then cooled, subsequent tests will always show a less elasticity at the higher temperature than at the lower, *if sufficient rest after cooling be allowed.* When, however, we come to such small molecular displacements as are involved in the passage of sound through a wire, even the apparent increase of elasticity, mentioned above as taking place at the first heating, vanishes. I have been able to prove that, when an iron or steel wire is thrown into longitudinal vibrations, so as to produce a musical note, the pitch of this note becomes *lower* as we *raise* the temperature even when the wire is heated for the first time*.

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[*] Phil. Trans. Part I., 1883, p. 130.

[†] *Ann. de Chimie et de Phys.* 3^me^ série, 1844, p. 421.

It seems rather strange that the error should have been so long allowed to remain uncorrected; for it has been known for many years that the pitch of a steel tuning-fork is lowered by small rises of temperature to a greater extent than would follow from mere change of dimensions. Calling the frequency of the fork n, we have†

$$n=\frac{\kappa b}{2\pi l^2}m^2, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where m is an abstract number,

b is the velocity of sound in steel,

l is the length,

κ the radius of gyration of the section about an axis perpendicular to the plane of bending.

If D be the thickness of the fork,

$$\kappa=\frac{D}{\sqrt{12}}.$$

We may therefore obtain

$$b=\frac{4\pi\sqrt{3}}{m^2}\frac{l^2}{D}n. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

From (2) and the value of the coefficient of thermal expansion of steel, it follows that if the pitch of the note is lowered by rise of temperature to the extent to which it is known to be, the velocity of sound *must* be lowered also. Indeed from the coefficient of thermal expansion of steel and from my own determination of the effect of change of temperature on the longitudinal elasticity of steel, I have calculated what would be the lowering of pitch of a certain fork, and find it in sufficient accord with the lowering of pitch as determined by direct experiment.

Wertheim inferred the increase of velocity of sound in iron and steel from the apparent increase of longitudinal elasticity produced by rise of temperature. From his experiments on the longitudinal elasticity of these metals I have collected the following :—

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* The *lowering* of pitch produced by *rise* of temperature was shown before the Society.

† Lord Rayleigh's 'Theory of Sound,' vol. i. p. 219.

Metal.	*Increase* per cent. of elasticity between 15° to 20° and 100° C.
Annealed iron	4·90
Annealed iron wire	6·91
Annealed cast steel	2·79
Annealed steel wire	23·20
Steel tempered blue	5·18

whereas my own experiments show that both the torsional and longitudinal elasticities of iron and steel are *decreased* by about 2½ per cent. when the temperature is raised from 0° C. to 100° C.

I have dwelt longer than I should otherwise have done on this part of my paper because I find that even our best text-books relating to Elasticity and Sound still retain what I am convinced is an error.

XXVI. *Measuring-Instruments used in Mechanical Testing.*

By Prof. W. C. Unwin, *F.R.S.*[*]

The determination of the exact distance between two fine marks on a standard of length is an operation of some difficulty, as is well known to physicists. But that operation is free from many of the difficulties which attend the measurements which have to be made in the engineering laboratory. Among these the determination of the modulus of elasticity (Young's modulus) of a bar by measuring its change of length by *stress* is one of the most important. Now the bars subjected to test are usually, in the part which can be measured, not more than 10 inches in length ; and the whole elastic extension of such a bar is generally only about 0·007 inch. It is obvious, therefore, that measurements must be made with considerable accuracy and refinement to be of any value. But the bar cannot be placed in a position convenient for measurement; and the attachments to the testing-machine are more or less in the way of the measuring-apparatus to be applied. The bar itself is a somewhat rough bar, the form of

[*] Read January 22, 1887.

which must not be interfered with to facilitate the measurements. Then also bars of very different forms have to be tested, flat and round, of various widths and diameters; and the measuring-apparatus must be applicable to all these with equal readiness. Last, but not least, the work of an engineering laboratory is pressing, and measurements must be carried out with rapidity.

In some cases, two diamond scratches have been made on the bar, and the distance between these measured by two micrometer-microscopes. Apparatus of this kind is awkward to apply on the testing-machine, and tedious to adjust and read.

A cathetometer has been used. But then two adjustments have to be made, and two readings taken for each elongation. Also the limit of accuracy of the cathetometer is hardly sufficient for the purpose.

Very often mechanical magnification by a lever is adopted. But there are some difficulties in satisfactorily attaching a lever-apparatus to the bar: if a leverage of 100 to 1 is adopted, the fulcrum distance becomes very short, and the range of the apparatus is limited. There is also some difficulty in the calibration of the instrument to determine the value of the readings.

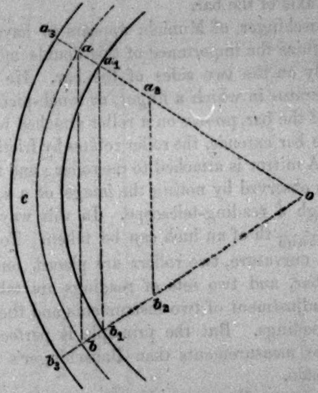
A micrometer-screw is sometimes used as a means of mechanical magnification. With this there is, again, the difficulty of suitable attachment to the bar; and, as generally used, it is difficult to ascertain when exact contact of the screw is obtained without excessive pressure.

There is a special difficulty in measuring the elongation of ordinary test-bars, which has been overlooked in the construction of most of the apparatus of this kind. It is difficult to get test-bars which are rigidly straight. Even if the test-bar is strictly straight, it is difficult to hold it in the testing-machine, so that the resultant of the stress on any cross section passes strictly through the centre of figure of the section. Now if this condition is not satisfied, the bar becomes curved during the test. The straightening of an initially curved bar, or the curving of an initially straight one, introduce errors in the measurements of very considerable amount.

If the measurements could be made at the axis of the bar, the errors of this kind with any amount of curvature likely to occur would not be very serious; but this is of course impossible. The best that can be done is to measure at the surface of the test-bar. But, in straightening, the surface of the bar on one side lengthens and on the other shortens, and thus introduces a not inconsiderable error of measurement. If, as in many forms of elongation measuring-apparatus, the measuring-points are two inches or more from the axis of the bar, the errors become very large relatively to the elongations to be measured.

Let fig. 1 represent a bar bent in the plane of the paper,

Fig. 1.



the centre of curvature being O. Then, if measurements could be made on the axis of the bar, between the points $a\,b$, the straightening of the bar would introduce an error equal to the difference of the length of the chord $a\,b$ and arc $a\,c\,b$. With any amount of curvature likely to occur in a test-bar, this error would not be very serious. Generally, however, the best that can be done is to measure the distance between points $a_1\,b_1$ on the surface of the bar. Then, since by straightening the lines a O, b O become parallel, the error introduced is the difference between $a_1 b_1$ and the arc $a c b$; and this is much more serious. Most commonly, however, measurements are made between points on clips fastened to the bar at 1 or 2 inches distance from its surface, such as $a_2 b_2$. Then the error introduced by straightening is the difference between a_2, b_2 and the arc $a c b$; and this may be a serious error, even with a very small amount of initial curvature.

If simultaneous measurements are taken of $a_1 b_1$ and $a_3 b_3$, the mean of these will have no greater error than the measurement of $a b$. That is, the mean of measurements on two sides of the bar reduces the error due to initial or induced curvature to the same amount as a measurement actually made at the axis of the bar.

Prof. Bauschinger, of Munich, appears to have been the first to recognize the importance of this double measurement symmetrically on the two sides of the bar. He has always used an apparatus in which a finger, or touch-piece, attached to one end of the bar, presses on a roller attached to the other end. As the bar extends, the roller rotates by friction against the finger. A mirror is attached to the roller; and the amount of rotation is observed by noting the image of a scale in the mirror through a reading-telescope. In this way measurements to $\frac{1}{125000}$th of an inch can be taken. To eliminate errors due to curvature, two rollers are placed, one on each side of the bar, and two sets of readings are taken. This involves the adjustment of two instruments and the taking of two sets of readings. But the principle is perfect; and no more accurate measurements than Bauschinger's have probably been made.

Touch-Micrometer Extensometer.—The first instrument used by the author was a kind of callipers. Two bars, one sliding in the other, could be set by touch to the distance between two fixed clips on the test-bar. A scale was engraved on silver on one bar; and the distance of the nearest division from a fixed zero-mark on the other was taken by a microscope-micrometer. Readings could be taken to $\frac{1}{10000}$th of an inch. The instrument is easy and rapid to use. Readings can be taken on both sides of the test-bar; and the readings are direct on to a carefully graduated scale, so that no calibration of the instrument is necessary.

Screw-Micrometer Extensometer.—This aims at obtaining the extension along the axis of the bar by a single reading. Two clips are fixed on the bar, each by a pair of steel points, one on each side, gripping the bar in a plane through its axis. If, then, these clips can be made to preserve the same relative position to the bar, the middle points of the clips will move in the same way as points on the axis of the bar. Fig. 2 is a diagrammatic sketch of the apparatus. *a a* and *b b* are the clips on the test-bar, fixed to it by points in its middle plane.

Fig. 2.

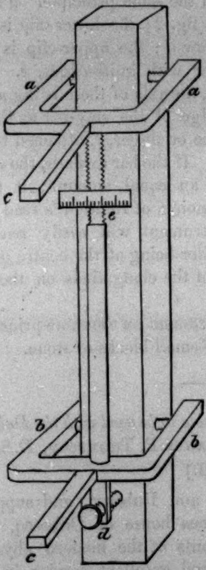
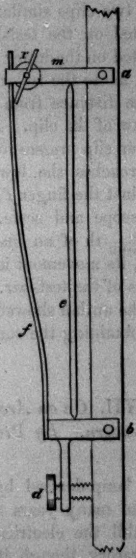


Fig. 3.



c c are projections on the clips, to which are fixed delicate spirit-levels; *d* is a small screw which just touches the test-bar;

e is a micrometer-screw with graduated head, which supports the upper clip on the lower clip. In use the lower clip is first levelled by the screw *d*; then the upper clip is levelled by the micrometer-screw, and a reading taken. The clips being always accurately levelled, in a plane perpendicular to that in which the four points attaching the clips to the test-bar lie, the micrometer-readings are the distances between the middle points of the two parallel clips; and their differences are the mean of the elongations on the two sides of the test-bar, or virtually are readings at the axis of the test-bar. Readings to $\frac{1}{10000}$th of an inch can be taken.

Roller-and-Mirror Extensometer.—Fig 3 is a diagrammatic sketch of another instrument on the same principle. *a* and *b* are two clips similar to those in fig. 2; the lower clip is supported on the test-bar by a screw *d*; the upper clip is supported on the lower by a stay-bar with knife-edges, *e*. At *r* and *m* are the roller and mirror, the axis of these being at the same distance from the knife-edge of the stay-bar as the set screw of the clip. A touch-piece or finger, *f*, attached to the lower clip presses on the roller. If the bar extends, the roller approaches the lower clip by an equal amount; it turns against the finger *f*; and the amount of rotation is read by a telescope and scale. This instrument will easily read to $\frac{1}{100000}$th of an inch. The roller being at the centre of the clip, its movement is the mean of the elongations on the two sides of the test-bar.

The author showed a third instrument on the same principle, for obtaining the compression of small blocks of stone.

XXVII. *On an Arc-Lamp suitable to be used with the Duboscq Lantern.* *By* Professor SILVANUS P. THOMPSON, *D.Sc.*[*]

[Plate III.]

THE lamp devised by Foucault and Duboscq, and supplied for so many years by the famous house of Duboscq, fails to fulfil the electrical requirements of the modern physical laboratory, though it has rendered excellent service in the past. Yet the lantern and optical adjuncts of the standard

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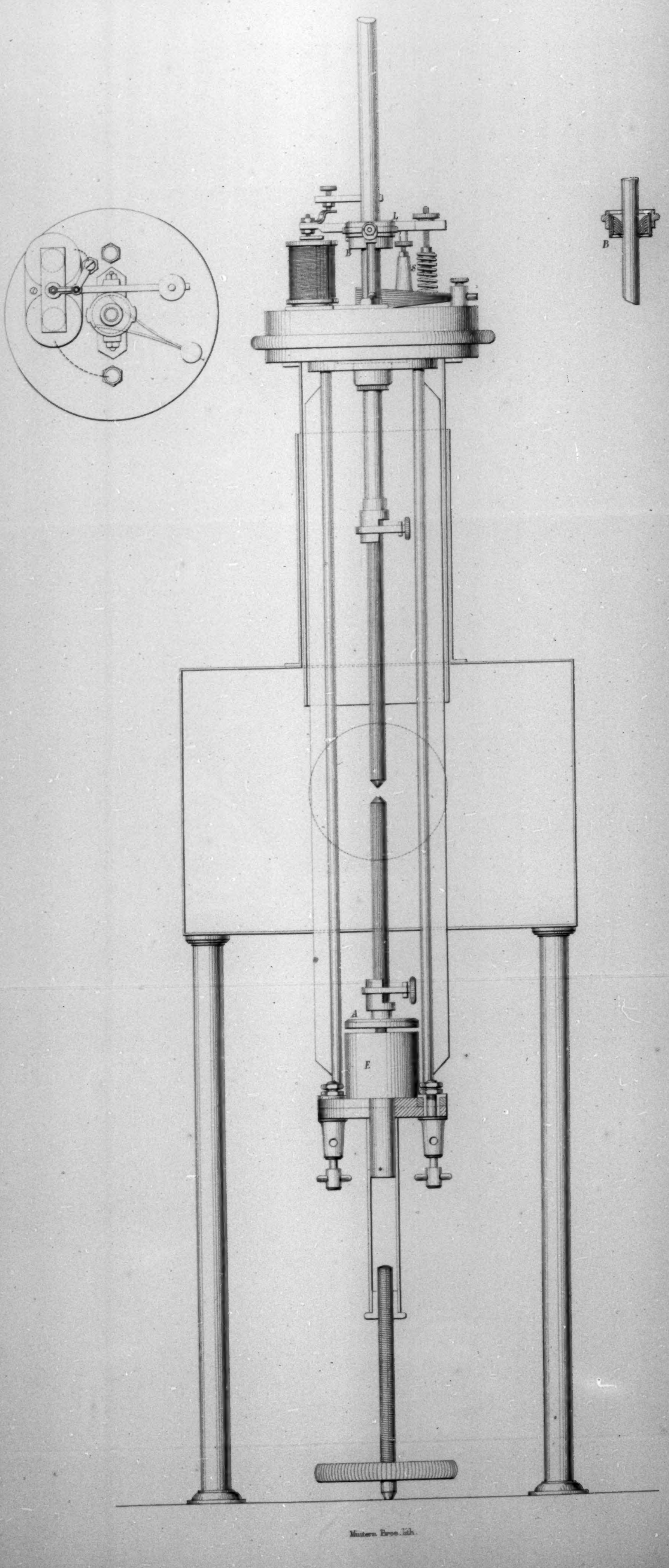
[*] Read March 27, 1886.



Mintern Bros. lith.

pattern of Duboscq are so widely used that it seemed desirable to find some other arc lamp which, while fulfilling the electrical requirements of the case, could be used with the Duboscq lantern.

Before describing the lamp which I have for twelve months employed for this purpose, I propose to state the conditions to be fulfilled, and the reasons why the old Duboscq lamp fails to fulfil them.

The modern physical laboratory is usually supplied with electric energy under one of two alternative conditions, namely either at constant potential or with constant current; more usually under the former condition. If supplied from a dynamo the dynamo may be either series-wound, shunt-wound, or compound-wound. If supplied from accumulators the accumulators will work at constant potential, and will have a very small internal resistance.

The arc-lamp for laboratory use must be capable of working under the given conditions. No doubt the Duboscq lamp worked fairly when supplied with current from 50 Grove's cells. But in a laboratory where there is another and better and less wasteful source of supply, 50 Grove's cells are not desirable. Though 40 accumulators have an electromotive force almost exactly equal to that of 50 Grove's cells, the Duboscq lamp does not work well with them unless a resistance of several ohms is intercalated in the circuit to represent the internal resistance of the Grove cells; and even then the Duboscq lamp does not, for certain reasons, work as satisfactorily as the lamp to be described, and its cost is about three times as great.

In every arc-lamp for optical purposes there must be mechanism adapted to perform the four following actions:—

1. To bring the carbons together into initial contact.

2. To part the carbons suddenly, and with certainty, to a short distance—about 3 millimetres—apart. This action is technically called "striking" the arc.

3. To supply carbon as fast as it is consumed, by moving one (or both) of the pencils forward into the arc. This action is called "feeding" the arc.

4. To so move the carbons, or their holders, that the luminous points retain the same position in space at the proper

focus of the optical system. This action is called "focusing" the arc.

It may be remarked, in passing, that the feeding mechanism of many lamps also performs the action, set down as No. 1 of the above, of bringing the carbons into initial contact preparatory to striking the arc.

In many arc-lamps the attempt is made to unite the striking and feeding mechanisms in one; but in many lamps, and in the one I have to describe, the striking and feeding mechanisms are distinct. The striking mechanism in all the arc-lamps of commerce consists of an electromagnet or solenoid arranged in the main circuit of the lamp, the armature or plunger of the same being mechanically connected with one or both of the carbons, so that when, by the turning on of the current through the touching carbons, there is a great rush of current, the attraction of the electromagnet or solenoid shall instantly part the carbons and strike the arc. In the majority of the commercial arc-lamps it is the upper carbon only that is raised to strike the arc; in a few other lamps, and in the one I am using, the lower carbon is depressed. In one of the older patterns of the Duboscq lamp the lower carbon was also thus directly acted upon, its holder being attached to the armature of an electromagnet beneath it. The same is true of the Serrin lamp. But in the Duboscq-Foucault lamp the arc is struck in a different way. The two carbon-holders are connected by racks to a clockwork gearing which either parts them or brings them together, the movement being driven by a double train of wheels, either of which can be released in turn. The weight of the upper carbon-holder drives the train that moves the carbons together; a coiled spring drives the train that parts the carbons. Whether either of the trains, or neither of them, shall be released is determined by the position of a double-toothed detent which, placed between the final spur-wheels of the two trains, locks both of them when in its mean position, but releases one or other when shifted to right or left. The position of this detent is determined by the current through the lamp, it being attached to one end of a three-arm lever, the two other ends of which are respectively attached to the armature of the controlling electromagnet and to an opposing spiral spring.

When the moment of pull of the electromagnet upon its armature is greater than that of the opposing spring, the detent is pulled over one way, releasing the approximating train of wheels while retaining locked the parting train. When the moment of the pull of the opposing spring exceeds that of the electromagnet on its armature, the detent is pulled over the other way, locking the approximating train and releasing the parting train. When the pull of the electromagnet exactly balances that of the opposing spring, both trains are locked. Now when the current is at first turned on, there is a sudden pull upon the armature of the electromagnet; but the carbons are not instantly parted, partly because of the inertia of the train of wheels, and partly because of the backlash of the mechanism. Two or three seconds may elapse before the arc is struck. This delay is serious, either when working with dynamo or with accumulators. If the dynamo is shunt-wound, the shortcircuiting even for this short period demagnetizes the field-magnets. If the dynamo is series-wound or compound-wound, or if accumulators are being used, there is overheating during the period of delay. Supposing, however, the arc to be struck, then the inertia of the train of wheels makes itself evident in another way; for it parts the carbons too far, producing a long arc of considerable resistance; and as the current then drops below its normal value, the armature goes over the other way, and the other train of wheels is momentarily released. This alternation between the two trains, which often lasts for some time, produces a disagreeable instability.

The feeding mechanism of arc-lamps next comes in for consideration. The object of the feeding mechanism is to supply carbon as fast as it is consumed, and so keep the light constant. But the light cannot be kept constant unless the consumption of electric energy in the arc is constant. The electric energy is the product of two factors—the current through the arc, and the difference of potential between the electrodes. Calling the current i and the potential difference e, it is the product ei which is to be kept constant. Now, as remarked at the outset, the very conditions of modern electric supply are that either e or i is maintained constant, the usual arrangement in commercial lighting being i constant for arc-lamps in series, and e constant for glow-lamps in parallel. One of the two factors being a constant by the conditions of the supply, the other factor must be kept constant by the feeding mechanism. Or, in other words, the variations of the other factor should be made to control the action of the feeding mechanism. The mechanical part of the feed may consist of a train of wheels driven by the weight of the carbon-holder or by a spring, or it may consist of a friction-clutch holding the carbon from sliding forward, or of a worm-gearing or any other; but it must be controlled by an electric mechanism of one of the two following kinds. For keeping i constant, the feeding mechanism must be controlled by an electromagnet (or solenoid) placed in the main circuit, working against an opposing spring or weight. For keeping e constant, the feeding mechanism must be controlled by an electromagnet (or solenoid) placed as a shunt to the arc, and working against an opposing spring or weight. In the latter case, if for any reason the arc grows too long, the potential at the terminals will rise, more current will flow around the shunt, which will then overcome its opposing spring (or weight), and will release the feeding machinery until balance is restored. The use of the shunt, introduced first by Lontin, enables arc-lamps to be connected two or more in series in one circuit. A less perfect solution is the differential principle introduced by Von Hefner Alteneck, where the difference between the attractions of a series and a shunt-solenoid maintains constant, not the product ei, but the difference $e-i$.

The only perfect solution of the problem is a feeding mechanism which, by combining in itself a shunt-coil and a series-coil, shall keep the product ei a constant, however either factor may vary. All the commercial arc-lamps for lighting in series have shunt-circuits to control the feeding mechanism; though often the arrangement takes the form of a shunt-coil wound (differentially) outside the series-coil of the striking mechanism; so that feeding is accomplished by the shunt-coil demagnetizing the striking electromagnet and momentarily un-striking the arc.

Returning to the Duboscq lamp, it may be observed that, as it possesses no shunt-coil, it can only feed by a weakening of the current in the main circuit. Hence it is obvious that a

Duboscq lamp cannot possibly work in a constant-current circuit. Also two Duboscq lamps will not work in series with one another, as their individual feeding is not independent of the other. Neither will two work in parallel with one another; for the weakening of current in one throws more current through the other, and the instability before alluded to—called "hunting" by electric engineers—becomes yet more pronounced.

The lamp that I have adapted to the Duboscq lantern is one known in commerce as the "Belfast" arc-lamp, its principles of construction being due to Mr. F. M. Newton; but I have had the design altered to suit the special work. In this lamp, as previously mentioned, the striking and feeding mechanisms are separate. The arc is struck by means of an electromagnet E of the tubular pattern, having as its armature an iron disk A, which, when no current is passing, is held up by a short spiral spring at about 3 millim. from the end of the electromagnet. The lower carbon-holder is mounted upon this disk, so that the arc is struck by the downward movement of the lower carbon. The feeding mechanism is both simple and effective. The upper carbon-holder is a long straight tube of brass: it passes through a collar in the frame of the lamp, and also through a metal box B above. This metal box contains a piece of curry-comb with the steel bristles of the comb set to point obliquely inwards and downwards. They grip the carbon-holder and allow it to be pushed downwards, but not upwards. The box itself is mounted upon a strong brass lever, L, close to the point of the lever. One end of this lever is drawn downwards by an adjustable spiral spring S, whilst the other carries an iron armature which stands immediately above the poles of an electromagnet, which is wound with fine wire and placed as a shunt to the lamp. Above the lever there is a contact-screw, platinum-tipped, making contact with the lever, exactly as in the ordinary trembling electric bell, and the lever and contact-screw are included in the shunt-circuit. The attraction of the shunt-magnet for its armature is opposed by the pull of the spiral spring. Whenever, by reason of the resistance of the arc, a sufficient current flows through the shunt-circuit, the opposing spring is overcome, and the lever is set into vibration like the lever of an electric bell, but more rapidly. The vibratory motion is thus communicated to the box containing the steel wire comb, which at once, by an action well known in mechanism, wriggles the carbon-holder downwards by innumerable small successive impulses. So soon as the motion of the carbon has reduced the resistance of the arc, the shunt-current diminishes and the feeding action ceases, to recommence when required. It is found best for lantern-purposes to send the current upwards through the lamp, the lower carbon being the positive one. A thick cored carbon of 13 to 15 millim. diameter is preferred, as it gives a good luminous crater and burns slowly. A 10-millim. copper-plated carbon is used for the upper electrode, and it is adjusted so that its centre falls slightly in front of the centre of the lower carbon, thereby causing the crater to send its light forward.

The lamp as used in commerce has no focusing-arrangement. In adapting it to the Duboscq lantern, the frame was made narrow; so that when the inner chimney of the Duboscq lantern was removed, the lamp could be dropped entire down the outer chimney, a metal sleeve of the same diameter as the inner chimney being added to the lamp as a guide. At the bottom of the lamp a gun-metal tube was added, tapped inside with a screw-thread, into which works a steel screw having a small hand-wheel near its lower end and a pointed pivot at the extremity. The lamp slides down the chimney of the lantern until the pivot touches the base-board. When the arc burns down the lower carbon, so that the luminous crater is no longer in the optical focus, a turn given by hand to the wheel suffices to raise it to the proper position; but the lamp will burn for ten minutes without requiring any readjustment on this account. The lamp shown to the Physical Society was constructed by Mr. E. Rousseau, Instructor in the Physical Workshop of the Finsbury Technical College, assisted by Mr A. D. Raine, now Demonstrator in the City and Guilds Central Institution.

XXVIII. *Note on the Tenacity of Spun Glass.*

By E. Gibson *and* R. A. Gregory [*].

It is well known that the tenacity of metallic wires increases as the diameter diminishes, so that very fine wires will carry much larger loads than those obtained by calculation based upon the assumption that the breaking weight varies as the square of the diameter. As glass can be drawn into very fine fibres, we have made some observations on the tenacity of this material, comparing the strength of very thin threads with that of rods made from the same glass, but of much greater thickness.

The experiments were carried out in the course of our work in the Physical Laboratory of the Normal School of Science and Royal School of Mines.

In dealing with a substance so brittle as glass, it is evident that special care must be taken to ensure that the observation is not vitiated by rupture due to a shearing stress, at or near the points of support. Precautions were taken to prevent this in all cases, and no experiments are quoted in this paper in which rupture took place near the points of support, or of attachment of the weight.

Three different thicknesses of glass were subjected to experiment: viz., fibres the diameters of which were about 0·002 and 0·004 centim. respectively, and rods with diameters varying between 0·05 and 0·09 centim.

The fibres were attached at the ends of two strips of paper by means of shellac varnish; this on setting was found sufficiently strong to carry more than the breaking weight, without allowing the fibre to slip. A small paper basket suspended from the lower strip carried the load, consisting of fine shot and silica, the latter being added when the fibre was near its breaking-point.

The diameter of the thread was measured at the place of rupture by means of a Compound Microscope with micrometer eye-piece. From data thus obtained the tenacity was calculated with the following results:—

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[*] Read February 12, 1887.

Diameter, in centims.	B. weight in grs.	Tenacity, in dynes per sq. centim.
0·00186	11·76	424×10^7
0·00159	8·70	425×10^7
0·00315	32·26	405×10^7
0·00340	43·23	466×10^7

Some observations were next made on rods about 1 millim. in diameter; the method of support and the loading being changed. Two pieces of angle brass, each about 8 inches long, were substituted for the slips of paper. Through a hole drilled near the end of the angles, a piece of ⅛″ wire was passed, turned up and soldered to the back. The free extremities of the wires were plaited into rings, which served to support the load and suspend the whole from a hook above.

The ends of the rod were laid in the angles, leaving the glass free for about 12 inches. Small pieces of red-ochre cement (a compound consisting of resin, red ochre, and bees-wax) were placed at intervals along the glass, and a Bunsen flame applied. The cement speedily melted, and imbedded the glass; on cooling, the whole was suspended vertically. A bottle was hung on the wire attached to the lower angle-piece, into which a fine stream of mercury flowed from a reservoir above. The apparatus was so arranged that when the rod broke mercury would no longer fall into the bottle.

The mode of measuring the diameters of the rods differed from that adopted in the case of the fibres. About half an inch of rod was broken away at the place of rupture, and mounted in wax on a piece of looking-glass, the broken section being upwards. Its diameter was then measured by means of a microscope-cathetometer, and the tenacity found as in the case of fibres. The following are the results of four experiments:—

Diameter, in centims.	Weight, in grs.	Tenacity, in dynes per sq. centim.
0·090	3908	60×10^7
0·082	4443	83×10^7
0·050	1948	97×10^7
0·042	1781	126×10^7

These observations show, in the first place, that the tenacity of fine fibres is very considerably greater than that of thick rods, and that the strength of rods increases as the diameter diminishes. It may be interesting to point out that the tenacity of glass fibres studied by us is nearly as great as that assigned by Wertheim to many of the metals; *e.g.*, the tenacity given by him for annealed steel wire 1 millim. in diameter is 499×10^7 cent.-dynes, and even in the case of drawn steel the tenacity is not greater than twice that of a glass fibre, viz. 998×10^7 cent.-dynes.

With steel pianoforte-wire the tenacity is, however, considerably greater; according to Sir William Thomson (Art. 'Elasticity,' *Encyc. Brit.*, new edition) the breaking-stress is

	Cent.-dynes.
Best pianoforte steel-wire	2318×10^7

The question as to what is the most probable cause of this increase in strength as the diameter diminishes presents some difficulty.

Quincke (*Sitzber. d. Ber. Acad.* 1868, p. 132) has suggested that the great increase observed in the case of metals is due to a surface tension, analogous to that observed in liquids. If this were the true explanation, the breaking-weight could be expressed by the sum of two terms which vary as the diameter and the square of the diameter respectively. This suggestion does not receive much support from our observations, as the results cannot be satisfactorily expressed by means of such a formula. It is, perhaps, more probable that the heating and rapid cooling undergone by the glass when it is drawn out into a fine fibre produces an increase in tenacity; and it is at all events certain that no comparisons can be made between the strengths of different materials unless they have undergone similar treatment, and unless the sizes of the rods or wires submitted to experiment are the same.

XXIX. *On Evaporation and Dissociation.*—Part VI.* *On the Continuous Transition from the Liquid to the Gaseous State of Matter at all Temperatures.* *By* WILLIAM RAMSAY, *Ph.D., and* SYDNEY YOUNG, *D.Sc.*†

[Plates IV., V., VI., & VII.]

IT was proved by Boyle, in 1662, that the volume of a gas, provided temperature be kept constant, varies inversely as the pressure to which it is subjected; this relation may be expressed by the equation $p=\frac{c}{v}$, or $pv=$ constant, where p and v respectively stand for pressure and volume. But subsequent experiments by Van Marum, Oersted, Despretz, and others showed that certain gases do not obey this law; and it is now well known that Boyle's statement is only approximate; for it has been proved by experiment by Regnault, Natterer, and more recently by Amagat, that no gas, under high pressures, is diminished in volume in inverse ratio to the rise of pressure. Indeed Boyle's law could hold only on the assumption that the actual molecules of matter possess no extension in space and exert no attraction on each other. A gas, such as hydrogen, at low pressures, and consequently at large volumes, fills a space very great when compared with the space occupied by the actual molecules; and these molecules are comparatively so distant from one another, that the attraction which they mutually exercise is inappreciable. But, on compression, the actual space occupied by the molecules bears an increased ratio to the space which they inhabit; and, by their approach, the attraction which they exert is also increased. The gas, then, deviates appreciably from Boyle's law.

Gay-Lussac, in 1808, enunciated the law that the volumes of all gases increase by a constant fraction of their volume at

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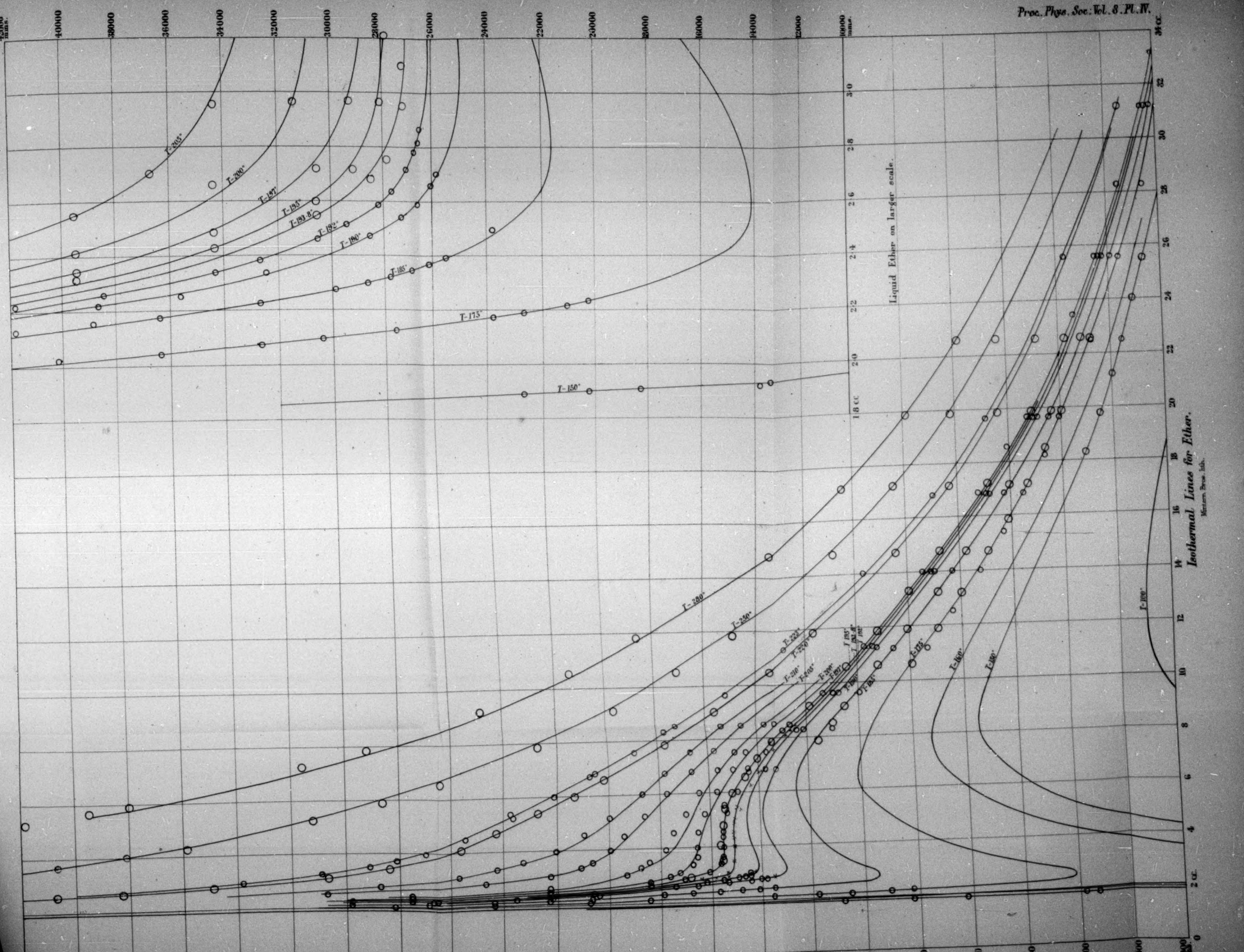
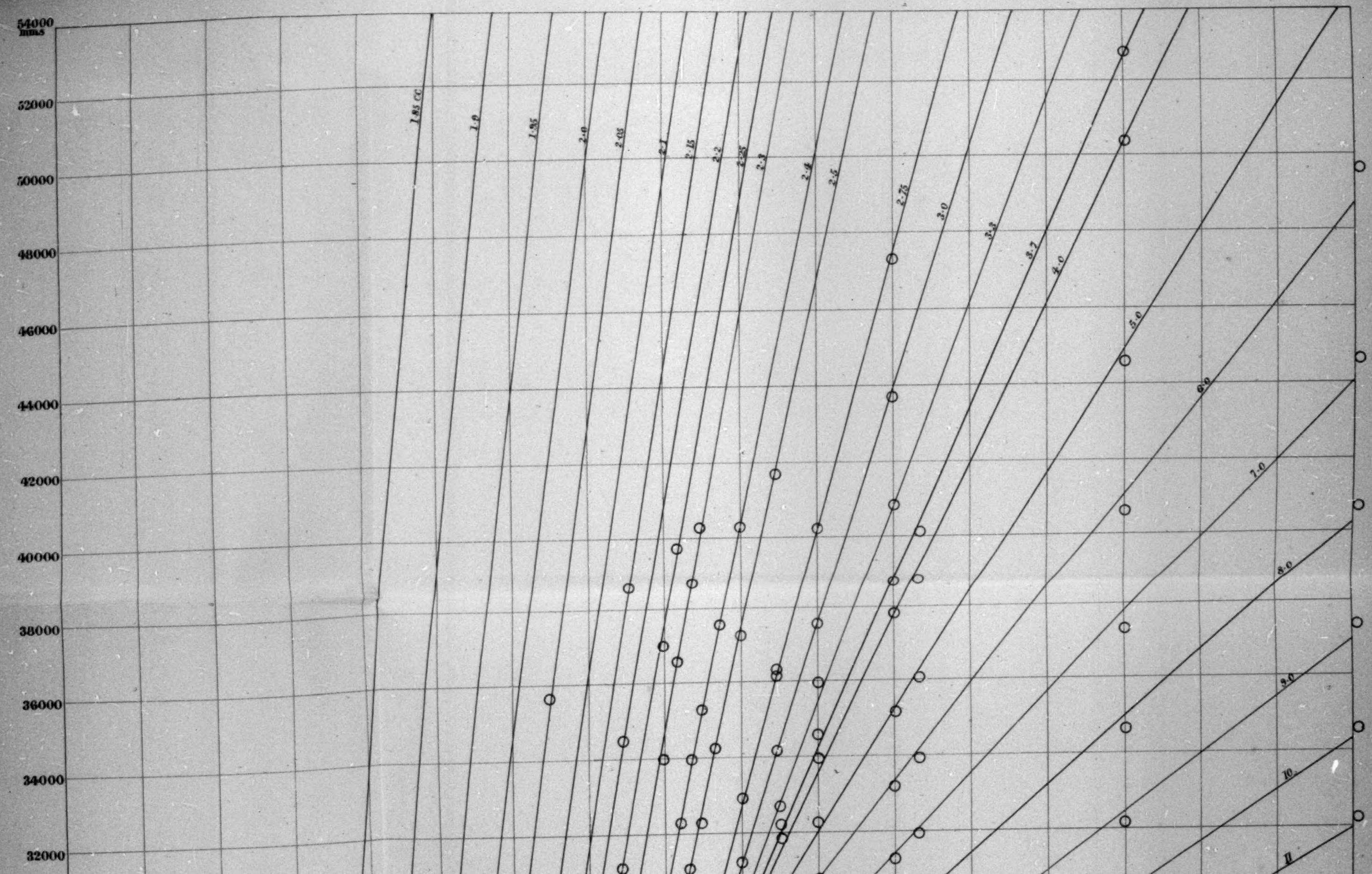
* Parts I. and II., Philosophical Transactions, part i. 1886, pp. 71 and 123; Part III., ibid. part ii., 1886, p. 1; Part IV., Trans. Chem. Soc. 1886, p. 790; Part V., in the hands of the Royal Society.

† Read February 26, 1887.



Isothermal Lines for Ether.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52000
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1·85 cc
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1·95
2·0
2·05
2·1
2·15
2·2
2·25
2·3
2·4
2·5
2·75
3·0
3·3
3·7
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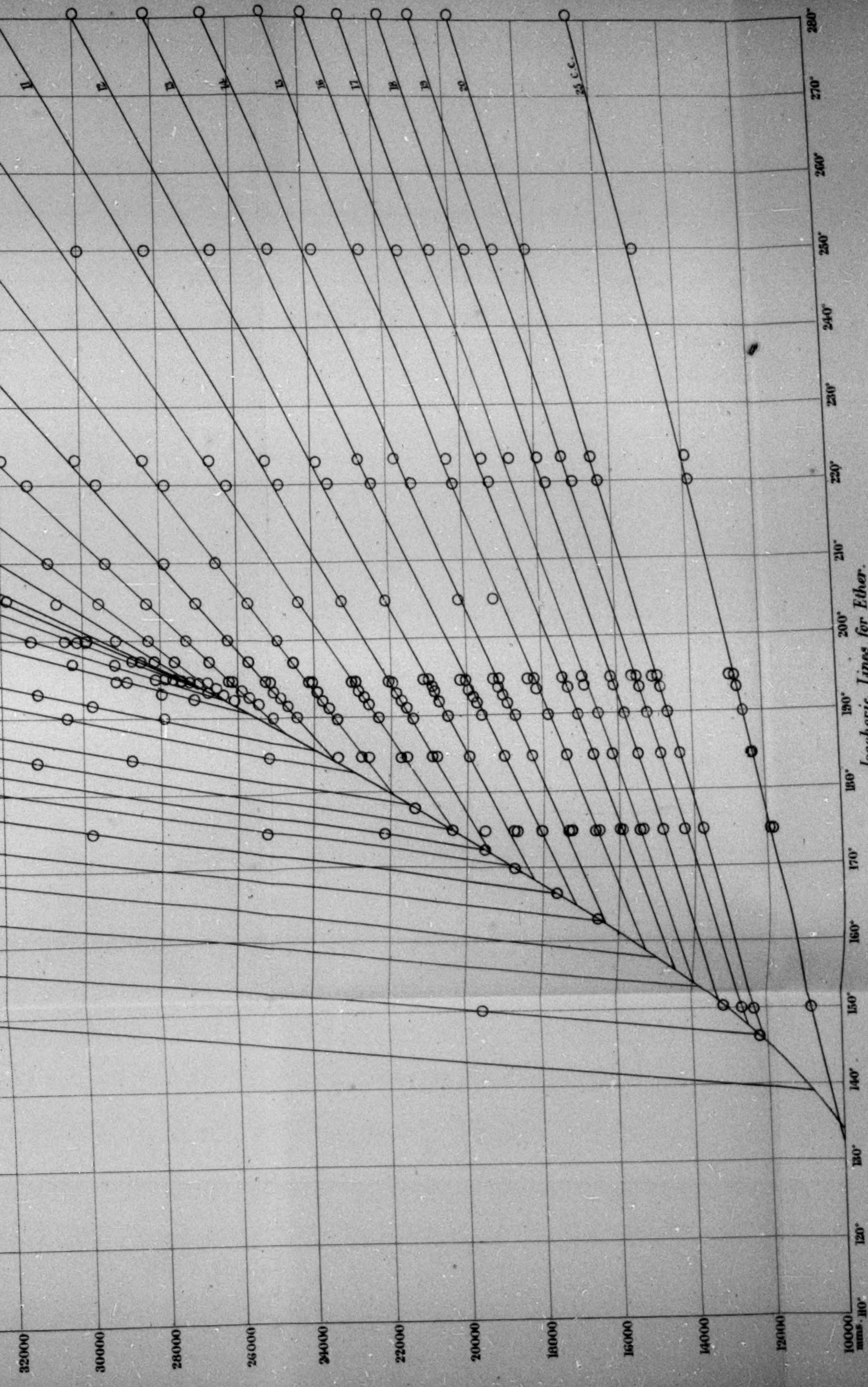
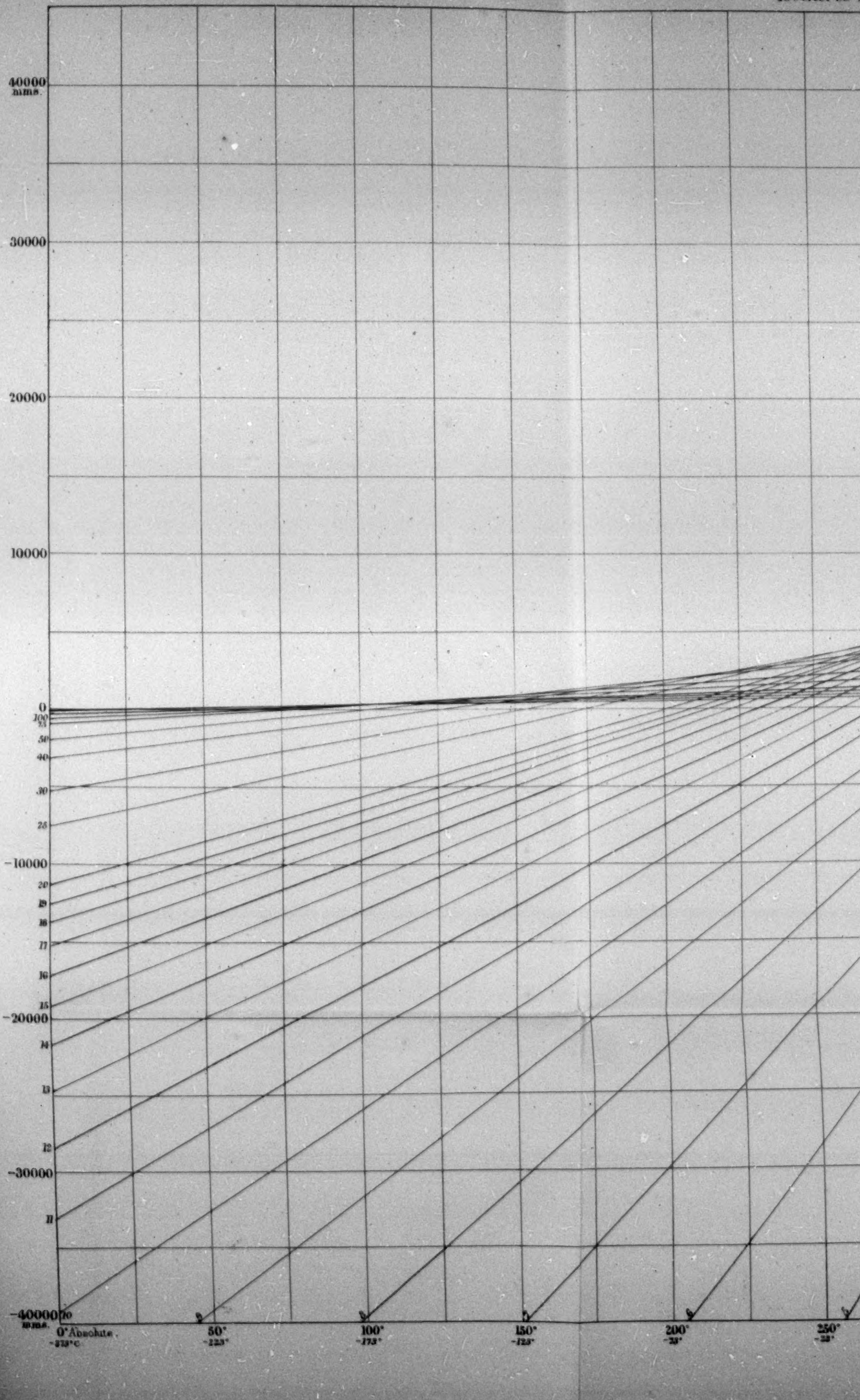
11



Isochoric Lines for Ether.

Mintern Bros. lith.

Isochoric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30000
20000
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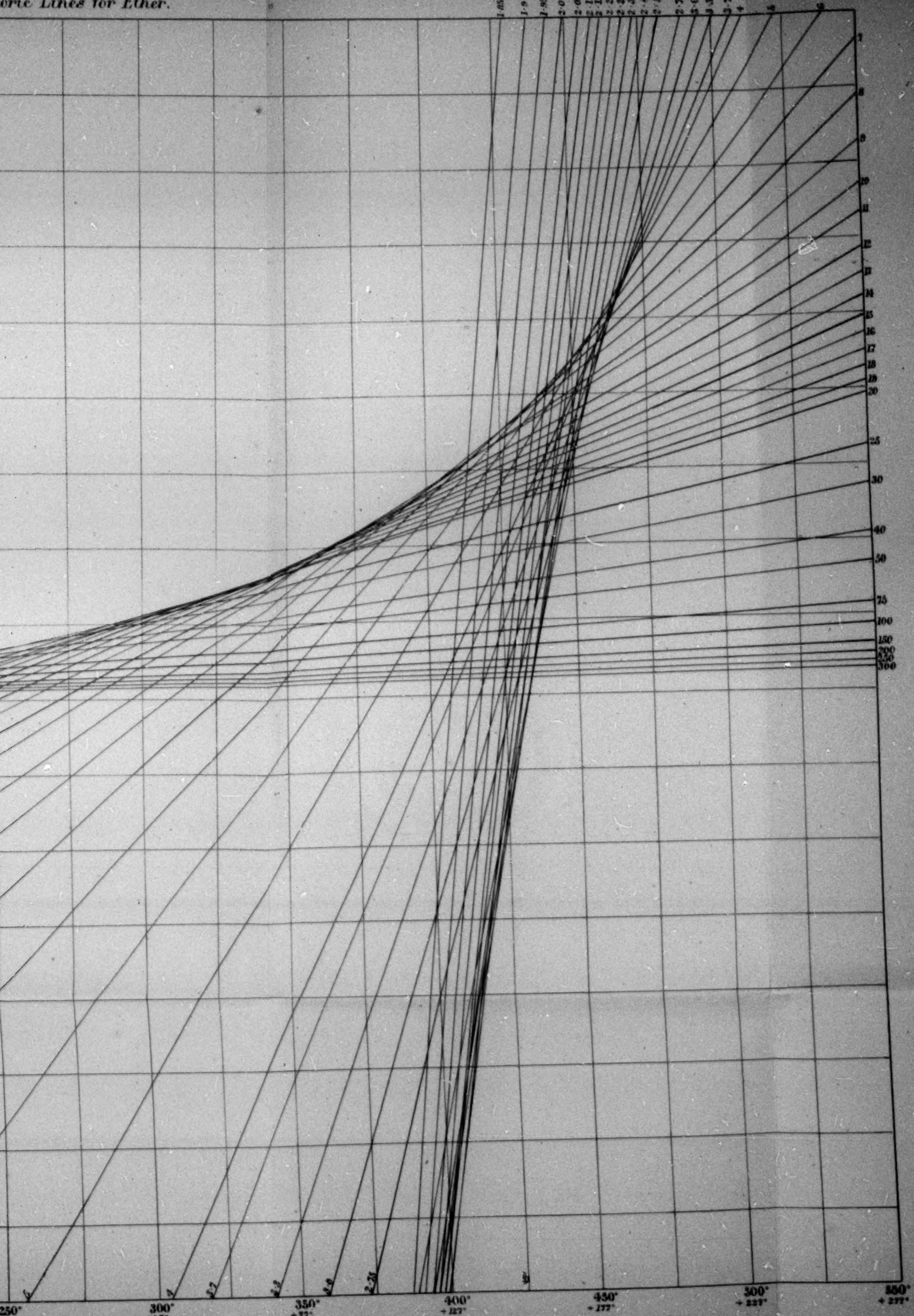
0
100
75
50
40
30
25
-10000
20
19
18
17
16
15
-20000
14
13
12
-30000
11
-40000 mms.
10
9
8
7
6
5
0° Absolute. -273°C
50° -223°
100° -173°
150° -123°
200° -73°
250° -23°

eric Lines for Ether.



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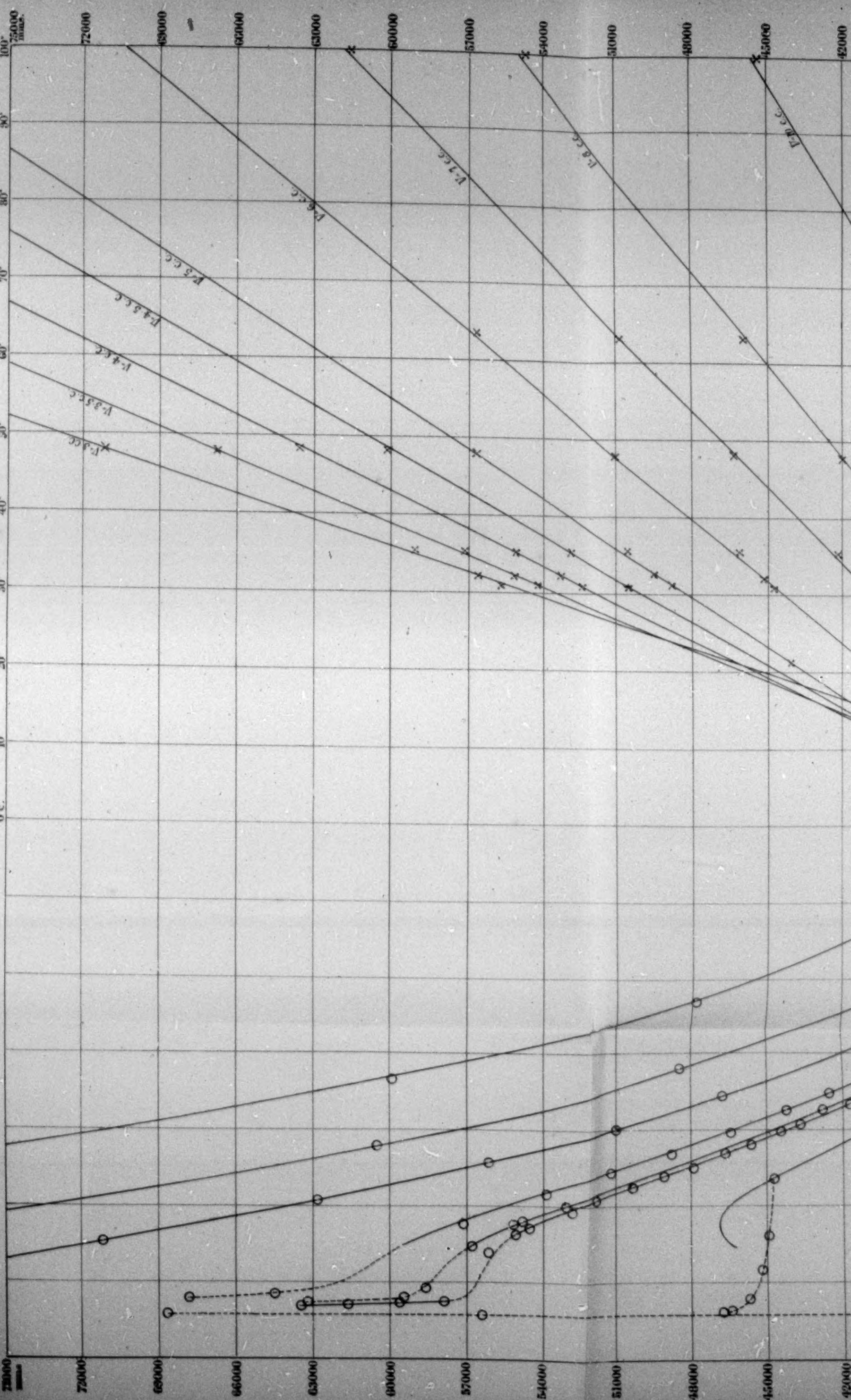
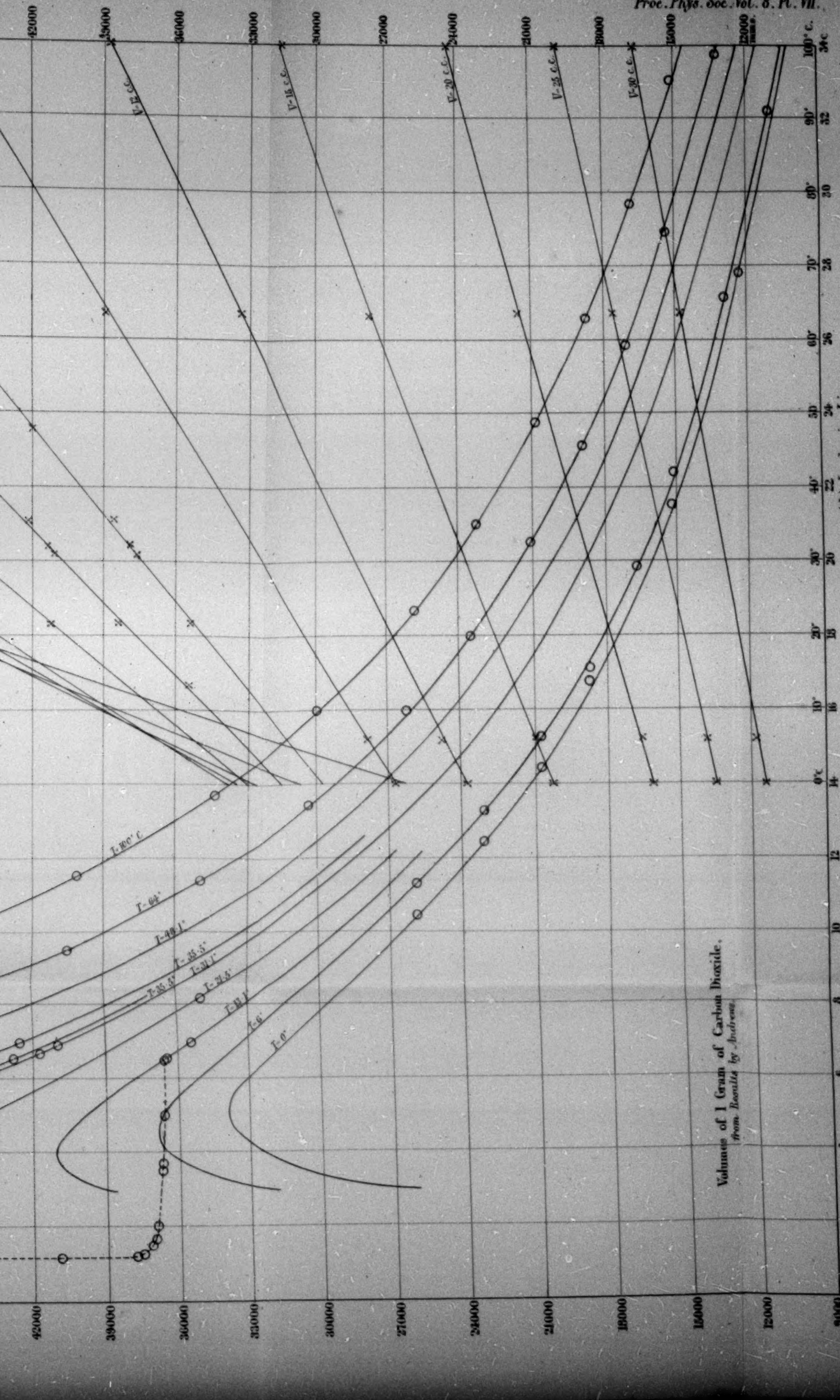


75000 mm.
72000
69000
66000
63000
60000
57000
54000
51000
48000
45000
42000
100°
90°
80°
70°
60°
50°
40°
30°
20°
10°
0°c.
V=3 c.c.
V=3.5 c.c.
V=4 c.c.
V=4.5 c.c.
V=5 c.c.
V=6 c.c.
V=7 c.c.
V=8 c.c.
V=10 c.c.



Volumes of 1 Gram of Carbon Dioxide, *from Results by Andrews.*

0° for each rise of 1° in temperature. It was subsequently ascertained by Magnus, and confirmed by Regnault, that certain gases deviate from this law, expanding more rapidly than others. Such gases, as a rule, are at temperatures not far removed from those at which they condense to liquids; that is, their volumes are comparatively small, and the actual size of the molecules and their mutual cohesion begin to manifest themselves within the range of experimental observation. Again, it is evident that no gas can perfectly follow Gay-Lussac's law; but the larger the volume it occupies the smaller is the influence of the disturbing factors. The usual expression for Gay-Lussac's law is $v=c(1+\alpha t)$, or, if the absolute temperature-scale be employed, $v=c\mathrm{T}$.

As a deduction from these laws, it follows that if the volume of unit mass of a gas, supposed to follow them rigorously, be kept constant, the pressure varies directly as the absolute temperature; or $p=c\mathrm{T}$.

Now, so long as the volume of unit mass of a gas is kept constant, the average distance of its molecules from one another will remain constant; and it is a fair assumption that the attraction of the molecules for each other will not vary. It may, of course, be the case that the effect of a rise of temperature on any individual molecule is to alter its actual volume; but of this we know nothing; and, in default of knowledge, it has been assumed by us that no such alteration takes place. If these assumptions are correct, it follows that the temperature and pressure of gases—and indeed the same assumptions may be extended to liquids—should then bear a simple relation to each other. We have obtained experimental proof of a convincing nature that this is the case; and in a preliminary note to the Royal Society, read on January 6, we promised such a proof. This proof is the subject of the present paper; and we must ask for indulgence in quoting a large array of figures, some of which have already been published, on the ground that such an important generalization requires as much experimental evidence as can be brought to bear on it.

The relation between the pressures and temperatures of a liquid or a gas at constant volume is expressed by the equation

$$p=bT-a;$$

where p is the pressure in millimetres, T the absolute temperature, and b and a constants. The values of these constants depend on the nature of the substance and on the volume. It follows from this, that if a diagram be constructed to express the relations of pressure, temperature, and volume of liquids and gases, where pressure and temperature form the ordinates and abscissæ, the lines of equal volume are straight*.

We have proved this to be the case for ethyl oxide (ether) between the temperatures 100° and 280°, and for volumes varying from 1·85 cubic centim. per gram to 300 cubic centim. per gram. This proof we now proceed to give.

The data for the calculations are at present in the press, and will shortly appear in the Philosophical Transactions for 1886, p. 10. A diagram (which will accompany that memoir) was constructed with the greatest care, showing isothermal lines, the ordinates and abscissæ being respectively pressures and volumes. It was possible to read pressure accurately to within 20 millim.; and volume, up to a volume of 3·1, to within 0·001 cubic centim. per gram; and, at volumes greater than 3·1 cubic centim. per gram, to 0·01 cubic centim. per gram. Pressures corresponding to each isothermal were then read off on the equal volume-lines, from curves constructed to fit the experimental points as accurately as could be drawn with the help of engineers' curves. These pressures and temperatures were then mapped as ordinates and abscissæ; and it was found that points corresponding to each volume lay in a straight line. Again, two points were chosen on these equal volume-lines, as far apart as the scale of the diagram would permit, and the values of the change of pressure per unit change of temperature, $\frac{dp}{dt}$, were ascertained for each separate volume chosen. To eliminate irregularities, these values were smoothed graphically; but it was difficult to find any very satisfactory method. The method employed for ether, which we found to give the best results, was to map as ordinates the ratios between these values, and similar values calculated on the supposition that the gas or liquid followed the usual gaseous laws, against the reciprocals of the volumes as abscissæ. A curve was then drawn, taking a mean course among the actual points, and the values of $\frac{dp}{dt}$ were calculated from readings at definite volumes. This expression, $\frac{dp}{dt}$, is the b of our formula. Having thus obtained the most probable value of b for each volume, the value of a at each volume was ascertained by calculation from each individual point read from the original curves, and at each volume the mean of all was chosen.

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* Amagat (*Comptes Rendus*, xciv. p. 847) has stated a similar relation for gases; his data are, however, imperfect, and he expressly states that the law does not apply to liquids.

Isothermals were then calculated by means of the equation $p = b\text{T} - a$, T being kept constant; and those values of a and b corresponding to the volumes required being selected. These calculated isothermals are shown on Plate IV.; and the lines of equal volume, or isochors*, on Plate V. It is evident, from inspection of the former, that the calculated lines correspond as closely as possible with the actual observations.

It is necessary now to give the data on which these deductions are based. The following Table gives those points corresponding to lines of equal volume read from the diagram constructed from experimental observations.

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* From ἴσος, *equal*, and χωρεῖν, *to contain*. Another suitable word would be "*isoplethe*," but we have Professor Jowett's preference for the one selected. Either of these terms seems preferable to that (*isometrics*) already proposed.

TABLE I.

Volume. cub. cent.										
1·9	P....	12340	19500							
	T....	145°·8	150°							
2·05	P....	16500	35700							
	T....	162°·7	175°							
2·10	P....	17700	29850							
	T....	166°·9	175°							
2·15	P....	18700	25260	38620						
	T....	170°·2	175°	185°						
2·20	P....	19560	22160	34160						
	T....	173°·05	175°	185°						
2·25	P....	20450	31070	36960	39750					
	T....	175°·9	185°	190°	192°					
2·3	P....	21250	28680	34000	36430	38600	40200			
	T....	178°·35	185°	190°	192°	193°·8	195°			
2·4	P....	25250	30380	32320	33980	35300	37500	40320		
	T....	185°	190°	192°	193°·8	195°	197°	200°		
2·5	P....	27920	29820	31230	32300	34200	37130	41580		
	T....	190°	192°	193°·8	195°	197°	200°	205°		
2·75	P....	26840	27970	28860	30270	32850	36240	40200	47200	
	T....	192°	193°·8	195°	197°	200°	205°	210°	220°	
3·0	P....	27270	28090	27900	29250	31230	34150	37440	43620	
	T....	193°	195°	195°	197°	200°	205°	210°	220°	
3·3	P....	27800	27740	28640	30550	32950	35960	40900		
	T....	195°	195°	197°	200°	205°	210°	220°		
3·7	P....	27640	27720	28470	30100	32240	34700	38840	40100	52700
	T....	195°	195°	197°	200°	205°	210°	220°	223°	250°

4	P....	27600	27690	28440	29900	31840	34050	37830	38900	50260							
	T....	195°	195°	197°	200°	205°	210°	220°	223°	250°							
5	P....	27000	27460	27460	28150	29250	30800	32400	35440	36140	44620						
	T....	193°·8	195°	195°	197°	200°	205°	210°	220°	223°	250°						
6	P....	26100	26400	26640	27000	26970	27560	28400	29700	30950	33260	33950	40580	49620			
	T....	192°	193°	193°·8	195°	195°	197°	200°	205°	210°	220°	223°	250°	280°·35			
7	P....	25130	25500	25750	25950	26210	26150	26670	27350	28400	29450	31340	31950	37330	44680		
	T....	190°	192°	193°	193°·8	195°	195°	197°	200°	205°	210°	220°	223°	250°	280°·35		
8	P....	23250	23380	24300	24660	24850	25060	25250	25190	25640	26200	27030	27930	29500	30100	34580	40750
	T....	185°	185°	190°	192°	193°	193°·8	195°	195°	197°	200°	205°	210°	220°	223°	250°	280°·35
9	P....	22540	22600	23400	23650	23830	23950	24130	24050	24450	24950	25650	26500	27810	28330	32160	37400
	T....	185°	185°	190°	192°	193°	193°·8	195°	195°	197°	200°	205°	210°	220°	223°	250°	280°·35
10	P....	21650	21790	22350	22650	22770	22870	23030	23000	23350	24400	26240	26670	30000	34590		
	T....	185°	185°	190°	192°	193°	193°·8	195°	195°	197°	205°	220°	223°	250°	280°·35		
11	P....	19550	19550	20800	20860	21450	21700	21800	21870	22020	21990	22270	23200	24820	25200	28170	32200
	T....	175°	175°	185°	185°	190°	192°	193°	193°·8	195°	195°	197°	205°	220°	223°	250°	280°·35
12	P....	18780	18800	19950	19990	20530	20740	20850	20930	21060	20990	22100	23540	23870	26510	30050	
	T....	175°	175°	185°	185°	190°	192°	193°	193°·8	195°	195°	205°	220°	223°	250°	280°·35	
13	P....	18050	18070	19130	19090	19650	19840	19960	20030	20130	20020	21100	22340	22740	25020	28200	
	T....	175°	175°	185°	185°	190°	192°	193°	193°·8	195°	195°	205°	220°	223°	250°	280°·35	
14	P....	17330	17400	18300	18300	18740	18960	19100	19200	19250	19190	20250	21240	21730	23770	26600	
	T....	175°	175°	185°	185°	190°	192°	193°	193°·8	195°	195°	205°	220°	223°	250°	280°·35	
15	P....	16670	16750	17570	17570	17970	18280	18500	18380	20250	22580	25190					
	T....	175°	175°	185°	185°	190°	193°·8	195°	195°	220°	250°	280°·35					
16	P....	16000	16100	16830	16850	17180	17500	17740	17610	19380	21460	23880					
	T....	175°	175°	185°	185°	190°	193°·8	195°	195°	220°	250°	280°·35					
17	P....	15440	15520	16180	16200	16530	16840	17030	16890	18540	20470	22730					
	T....	175°	175°	185°	185°	190°	193°·8	195°	195°	220°	250°	280°·35					

Table I. (*continued*).

Volume. cub. cent.													
18	P....	13350	14880	14940	15580	15600	15900	16270	16330	16210	17780	19600	21640
	T....	150°	175°	175°	185°	185°	190°	193°·8	195°	195°	220°	250°	280°·35
19	P....	12840	14370	14390	15020	15020	15330	15570	15720	15610	17040	18780	20670
	T....	150°	175°	175°	185°	185°	190°	193°·8	195°	195°	220°	250°	280°·35
20	P....	12240	13880	13880	14500	14480	14790	15000	15130	15020	16400	18000	19800
	T....	150°	175°	175°	185°	185°	190°	193°·8	195°	195°	220°	250°	280°·35
25	P....	10700	11800	11860	12280	12330	12500	12730	12800	12760	13820	14960	16440
	T....	150°	175°	175°	185°	185°	190°	193°·8	195°	195°	220°	250°	280°·35
30	P....	9350	10220	10600	10780	10960	11050	11970					
	T....	150°	175°	185°	190°	193°·8	195°	223°					
40	P....	7430	8030	8340	8460	8560	8600	9330					
	T....	150°	175°	185°	190°	193°·8	195°	223°					
50	P....	6150	6620	6840	6940	7010	7020	7600					
	T....	150°	175°	185°	190°	193°·8	195°	223°					
75	P....	3650	4290	4600	4730	4800	4860	5210					
	T....	100°	150°	175°	185°	190°	195°	223°					
100	P....	2820	3280	3500	3600	3680	3710	3950					
	T....	100°	150°	175°	185°	190°	195°	223°					
150	P....	1695	2509										
	T....	59°·7	195°										
200	P....	1260	1897										
	T....	50°	195°										
250	P....	1020	1525										
	T....	50°	195°										
300	P....	860	1275	1368.									
	T....	50°	195°	223°									

Lines of equal volume, or isochors, were then mapped from these results, pressures and temperatures being ordinates and abscissæ. The values of $\frac{dp}{dt}$, or b, were then read for each separate volume and smoothed, as before described. The following Table shows the read values, and the values after smoothing. The values of a are also given, calculated by the equation $a = bt - p$, from the results shown on the previous table; the means of all the individual results for each volume are stated.

TABLE II.

Volume.	*b* found.	*b* calculated.	log *b*.	*a*.
1·85	......	2034	3·30826	826860
1·90	1746	1861	3·26986	767670
1·95	......	1716	3·23452	715860
2·0	......	1597	3·20335	672820
2·05	1561	1492	3·17372	633070
2·1	1500	1405	3·14777	600110
2·15	1342	1320	3·12061	566170
2·2	1211	1243	3·09462	535100
2·25	1155	1175	3·07022	507170
2·3	1117	1115	3·04744	482160
2·4	1020	1010	3·00423	437240
2·5	920·8	919·7	2·69363	397970
2·75	732·0	732·0	2·86451	313605
3·0	623·5	621·7	2·79357	262917
3·3	535·7	532·8	2·72659	221630
3·7	453·1	454·6	2·65762	185109
4·0	413·7	413·7	2·61669	165996
5·0	321·5	319·1	2·50392	121895
6·0	257·15	254·2	2·40511	91906
7	213·6	208·7	2·31959	71464
8	178·0	176·1	2·24584	57203
9	150·95	151·4	2·18022	46742
10	130·8	132·7	2·12280	39079
11	116·25	117·6	2·07027	33037
12	104·45	105·5	2·02336	28401
13	94·29	95·54	1·98017	24659
14	85·00	87·09	1·93998	21567
15	78·82	80·06	1·90339	19125
16	72·29	73·95	1·86893	17049
17	67·53	68·76	1·83733	15313
18	62·53	64·24	1·80780	13854
19	59·23	60·11	1·77893	12533
20	55·70	56·43	1·75151	11386
25	43·75	43·26	1·63612	7529
30	35·60	34·99	1·54393	5412
40	26·23	25·09	1·39945	3159
50	20·38	19·46	1·28925	2077
75	12·82	12·50	1·09674	994
100	9·32	9·119	0·95997	571
150	5·87	5·923	0·77254	270
200	4·38	4·396	0·64306	160·5
250	3·46	3·483	0·54198	105
300	2·93	2·858	0·45605	59

TABLE III.

V.	0°	100°	150°	160°	175°	185°	190°	192°	193°·8	195°	197°	200°	205°	210°	220°	223°	250°	280°
	mm.	mm.	mm.	mm.	mm.	mm.	mm.	mm.	mm.	mm.	mm.	mm.	mm.	mm.	mm.	mm.	mm.	mm.
1·85	−271700	−68330	+33340	+53680														
1·9	−259490	−73330	19740	38360														
1·95	−247390	−75790	10110	27180														
2·0	−236800	−77070	2780	18760	42720													
2·05	−225800	−76710	−2020	12900	35270													
2·1	−216460	−75930	−5670	8390	29470	43530												
2·15	−205780	−73770	−7660	5440	25240	38450	45040	47680	50060									
2·2	−195650	−71300	−9130	3310	21960	34400	40610	43090	45330									
2·25	−186260	−68710	−9940	2880	19450	31210	37080	39430	41550	42970								
2·3	−177650	−66110	−10340	820	17550	28710	34280	36510	38520	39860	42090							
2·4	−161750	−60590	−10100	0	15150	25250	30290	32310	34130	35340	37360	40390						
2·5	−146900	−54930	−8950	250	14040	23240	27830	29670	31330	32440	34280	37030	41630	46230				
2·75	−113700	−40490	−3900	3429	14410	21730	25380	26850	28170	29050	30510	32710	36370	40030	47350	49540		
3·0	−93135	−30965	+ 115	6335	15665	21875	24985	26225	27345	28095	29335	31205	34315	37425	43635	45495		
3·3	−76170	−22880	3760	9080	17080	22410	25070	26130	27100	27740	28800	30400	33070	35730	41060	42650		
3·7	−61110	−15550	7180	11730	18550	23090	25360	26270	27090	27640	28550	29910	32190	34460	39060	40370	52640	

4	−53056	−11686	9004	13144	19344	23484	25544	26374	27124	27624	28444	29684	31754	33824	37964	39204	50374	
5	−34783	−2875	13085	16275	21065	24255	25845	26485	27055	27445	28085	29035	30635	32225	35425	36375	44995	54565
6	−22520	+2897	15604	18144	21954	24504	25774	26274	26734	27044	27554	28314	29584	30854	33394	34164	41024	48644
7	−14480	6393	16830	18918	22049	24136	25179	25596	25972	26224	26636	27266	28311	29356	31446	32061	37706	43966
8	−9119	8495	17301	19063	21705	23467	24346	24698	25016	25228	25580	26108	26989	27870	29641	30158	34914	40200
9	−5481	9743	17314	18829	21100	22615	23371	23674	23947	24129	24432	24886	25643	26401	27915	28369	32457	37001
10	−2858	10410	17044	18371	20361	21688	22351	22616	22855	23015	23280	23678	24342	25005	26332	26729	30311	34293
11	− 943	10814	16692	17868	19631	20807	21394	21629	21841	21983					24922	25274	28448	31976
12	+ 407	10960	16237	17292	18875	19930	20457	20668	20859	20986					23624	23940	26789	29956
13	1422	10976	15753	16709	18142	19097	19574	19765	19937	20053					22441	22727	25307	28173
14	2209	10929	15273	16144	17451	18322	18757	18931	19088	19193					21370	21631	23982	26596
15	2730	10736	14738	15539	16740	17541	17941	18100	18245	18341					20343	20582	22744	25146
16	3139	10534	14231	14971	16080	16820	17189	17337	17470	17559					19408	19629	21626	23845
17	3458	10334	13772	14460	15491	16179	16522	16660	16784	16867					18586	18791	20648	22711
18	3683	10107	13319	13962	14925	15568	15889	16017	16133	16210					17816	18009	18743	21671
19	3876	9887	12903	13494	14395	14997	15297	15417	15525	15598					17100	17280	18903	20707
20	4019	9662	12478	13048	13895	14459	14741	14854	14955	15023					16434	16606	18127	19820
25	4282	9608	10771	11204	11853	12286	12502	12588	12666	12718					13800	13930	15098	16396
30	4140	7639	9388	9738	10263	10613	10788	10858	10921	10963					11838	11942	12887	13937
40	3690	6199	7453	7704	8080	8331	8456	8506	8552	8582						9284		
50	3237	5183	6227	6351	6643	6838	6935	6974	7009	7033						7578		
75	2417	3667	4291	4416	4604	4729	4791	4816	4839	4854						5244		
100	1919	2831	3287	3378	3515	3606	3651	3670	3686	3697						3952		

The lines of equal volume calculated from these values of *a* and *b* are reproduced graphically in Plates V. and VI. We propose to discuss the form of the diagram later.

We have calculated the values of p for various isothermals, at the above volumes. These are shown in Plate IV.; the actual experimental observations, of which a detailed account is given in the 'Philosophical Transactions,' 1886, p. 10 *et seq.*, are represented by circles. It is evident that the curves through the calculated points represent the actual measurements very closely, indeed as nearly as unavoidable error of experiment allows. It is to be noticed that the greatest divergence is at the temperatures 250° and 280°, but the deviations are in opposite directions, and must therefore be ascribed to experimental error.

Table III. (pp. 202, 203) gives the data from which the calculated isothermals were constructed.

As volumes above 30 cubic centim. per gram are not given in the diagram, we have thought it advisable to show the correspondence of calculated and observed results by a table; the calculated numbers were read from curves specially constructed from the formula $p=bt-a$, and the observed results are those actually furnished by our experiments. It will be seen that the correspondence is very close.

Table III. (*continued*).

Temperature 100°.

Volume.	Pressure found.	Pres. calculated.	Volume.	Pressure found.	Pres. calculated.
c. c.	millim.	millim.	c. c.	millim.	millim.
54·06	4817	4875	74·42	3668	3685
55·50	4720	4760	77·34	3546	3550
56·95	4627	4670	83·14	3334	3320
59·84	4434	4470	86·02	3243	3215
62·73	4265	4290	88·89	3150	3120
65·63	4102	4100	94·63	2978	2970
68·56	3946	3970	97·51	2893	2900
71·48	3818	3815			
Temperature 150°.					
31·09	9066	9110	68·64	4651	4675
33·94	8497	8520	74·51	4304	4310
39·66	7484	7505	80·35	4027	4010
45·43	6674	6745	86·13	3783	3760
51·23	6024	6100	91·87	3564	3530
57·02	5480	5560	97·63	3375	3345
62·81	5034	5090			

Table III. (*continued*).

Volume.	Pressure found.	Pres. calculated.	Volume.	Pressure found.	Pres. calculated.
Temperature 175°.					
c. c.	millim.	millim.	c. c.	millim.	millim.
31·11	9906	9975	68·69	4987	5000
33·96	9248	9290	74·56	4626	4630
39·68	8065	8130	80·40	4307	4310
45·46	7208	7205	86·18	4035	4030
51·26	6485	6510	91·93	3803	3800
57·06	5903	5940	97·69	3589	3600
62·85	5396	5450			
Temp. 185°.			**Temp. 190°.**		
31·12	10284	10300	31·12	10455	10460
45·47	7434	7460	45·47	7549	7545
59·97	5811	5865	59·97	5902	5940
74·58	4755	4770	74·59	4828	4810
86·21	4159	4140	86·21	4210	4190
91·95	3915	3900			
97·72	3692	3690			
Temp. 192°.			**Temp. 193°·8.**		
31·12	10544	10520	31·12	10587	10590
45·48	7590	7600	45·48	7627	7630
59·98	5930	5970	59·98	5951	6000
74·60	4847	4850	74·60	4867	4875
86·42	4230	4200	86·42	4252	4220
Temp. 195°.			**Temp. 197°.**		
31·12	10631	10620	33·17	10108	10055
45·48	7651	7675	38·07	8972	8965
59·98	5969	6020	47·84	7312	7320
74·60	4884	4895	57·59	6166	6130
86·42	4260	4230	67·33	5356	5340
91·97	4007	4000	77·05	4718	4735
97·74	3797	3775	86·75	4219	4220
			96·44	3820	3820
Temperature 223°·25.					
31·15	11567	11550	80 50	4870	4880
45·51	8260	8240	86·29	4556	4550
60·02	6412	6420	92·04	4289	4270
74·65	5232	5225	97·81	4044	4020

These complete the data for ether. It appeared necessary to examine the relations between volume, temperature, and pressure for carbon dioxide, because it is chemically entirely different from ether, and also because the data are furnished by Dr. Andrews, whose experimental skill was very great; and we shall prove that his results entirely corroborate our views.

It was first necessary to correct the pressures given by him in atmospheres by means of Amagat's results, so far as that is possible. As Amagat's experiments on the compressibility of dry air do not extend beyond 65,000 millim., no correction was possible above that pressure; and extrapolation is inadmissible, inasmuch as the minimum value of *pv* for air is at 60,000 millim.

Data for obtaining the actual volume of carbon dioxide used are given by Andrews. The weight was calculated in the following manner:—Andrews gives the volume of carbon dioxide filling his tubes at 0° and 076 millim., and from Regnault's data the weight was calculated. This refers to Andrews's first paper (Phil. Trans. 1869, ii. p. 575). In his second paper (Phil. Trans. 1876, p. 421) no direct data are given from which the weight can be determined; but we succeeded, by combining the results given in his various tables, in arriving at the weight without any serious error. His results are reproduced in an available form in the following Tables.

TABLE IV. (The first quantity weighed 0·000612 gram.)

Temp. 13°·1.		Temp. 21°·5.		Temp. 31°·1.	
P.	Vol. of 1 gram.	P.	Vol. of 1 gram.	P.	Vol. of 1 gram.
millim.	c. c.	millim.	c. c.	millim.	c. c.
68726 *	1·038	46600	1·232	63462	1·389
56333	1·059	46383	1·241	61416	1·425
40725	1·104	45490	1·484	59540	1·470
37631	1·124	45155	2·270	57847	1·495
37459	1·145	44962	3·124	56178	1·812
37074	1·377	44787	4·760	55010	2·234
36942	1·547	34907	8·118	54588	2·338
36816	1·972			53089	3·814
36719	2·758			51709	4·192
36668	3·733			50390	4·534
36610	5·004			49118	4·855
36528	6·554			47910	5·147
36433	6·595			46725	5·471
35497	6·964			45622	5·750
				44577	6·009
				43611	6·265
				43182	6·515
				41761	6·765
				40895	7·003

* The pressures to which an asterisk is affixed are not corrected.

Table IV. (*continued*).

Temp. 32°·5.		Temp. 35°·5.		Temp. 48°·1.	
P.	Vol. of 1 gram.	P.	Vol. of 1 gram.	P.	Vol. of 1 gram.
millim.	c. c.	millim.	c. c.	millim.	c. c.
63246	1·461	81775 *	1·330	83144 *	1·999
59425	1·612	75673 *	1·392	72344 *	2·999
58501	1·818	70406 *	1·476	62837	4·061
56813	2·954	68035 *	1·532	56311	5·057
55151	3·543	64516	1·624	51012	5·991
54839	3·629	60552	2·511	46675	6·887
53292	4·034	57057	2·549		
42808	6·595	53977	4·283		
		51166	4·831		
		48625	5·396		
		46340	5·935		
		44263	6·432		
		42383	6·917		

Table IV. (*continued*).

(The weight of the second quantity was 0·0018075 gram.)

Temp. 0°.		Temp. 6°–6°·9.		Temp. 63° 6–64°.		Temp. 99°·5–100°·7.	
P.	Vol. of 1 gram.	P.	Vol. of 1 gram.	P.	Vol. of 1 gram.	P.	Vol. of 1 gram.
millim.	c. c.	millim.	c. c.	millim.	c. c.	millim.	c. c.
25865	10·53	25870	11·25	169420*	1·401	169910 *	1·816
23325	12·36	23291	13·09	110610*	1·907	110530 *	3·161
20800	14·53	20822	15·16	81229*	3·363	80323 *	5·057
18674	16·77	18681	17·11	60422	5·477	59985	7·192
15155	21·73	16777	19·90	48425	7·485	47910	9·391
12277	27·83	15161	22·54	40554	9·462	40169	11·52
9081	39·09	12907	27·16	34806	11·45	34382	13·72
		11093	32·18	30351	13·48	29910	15·96
		9994	36·12	26212	15·99	25930	18·74
		9087	40·06	23568	18·00	23325	21·03
				21106	20·41	20876	23·70
				18866	23·08	18711	26·65
				17000	25·86	16858	29·74
				15356	28·88	15214	33·09
				13288	33·74	13153	38·58

As with ether, these numbers were plotted graphically up to a pressure of 75,000 millim. Above 65,000 millim. no true correction for deviation of Andrews's air-gauge was possible;

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* The pressures to which an asterisk is affixed are not corrected.

but approximate corrections were introduced. It was possible to read pressures to within 30 millim. on the scale employed, and volume to within 0·02 cub. centim. per gram. Pressures corresponding to even volumes were read off, as with ether; and on mapping the isochors with temperatures as abscissæ and pressures as ordinates, the resulting points lay in straight lines. The values of b, i. e. of $\frac{dp}{dt}$, were then read off, and smoothed, by mapping them against the reciprocals of the volumes. After smoothing, the values of a were calculated at each volume, making use of the pressures previously read from the curve representing isothermals. The diagram (1) on Plate VII. was then constructed from these smoothed values. The crosses denote our readings of pressures at the temperatures chosen by Andrews for his isothermals. These values of a and b were then made use of in recalculating isothermals at the above temperatures, and the diagram (2) on Plate VII. represents the curves complete so far as Andrews's data allow. The circles represent Andrews's actual measurements; and it is evident that no better concordance could be expected. The tables which follow give the data afforded by Andrews's experiments.

TABLE V.

Pressures read from Curves originally drawn from Andrews's experimental data, and represented by circles in the diagram (2), Plate VII.

Vol.	Temperature.									
	0°.	6°.	13°·1.	21°·5.	31°·1.	32°·5.	35°·5.	48°·1.	64°.	100°.
c. c.	mm.	mm.	mm.	mm.	mm.	mm.	mm.	mm.	mm.	mm.
30	11430	11790	...	...	...	...	...	...	14820	16710
25	13480	13830	...	...	...	...	...	...	17500	19860
20	16200	16570	...	...	...	...	...	...	21450	24300
15	20300	20970	...	...	...	...	...	...	27700	31570
12	23730	24800	...	...	...	...	...	...	33500	38730
10	26715	28000	...	...	...	...	...	...	38970	45330
8	...	...	...	35340	37560?	37800?	38400?	41930	46200	54630
7	...	...	35340	38220?	40970	41370	42060	46200	50850	61500
6	...	...	...	41100?	44700	45060	46000	51000	56700	
5	...	...	...	44100?	48600	49200	50370	56760		
4·5	...	...	...	...	50550	51400	52830	60000		
4·0	...	...	...	...	52420	53430	55140	63500		
3·5	...	...	...	...	54250	55260	57240	67000		
3·0	...	...	...	...	55800	56700	59130	72400		

TABLE VI.

Read and Smoothed Values of *b*, and Values of *a*.

Vol.	*b*, read.	*b*, smoothed.	log *b*.	*a*.
c. c.				
30	52·3	52·5	1·72016	2877
25	63·3	64·0	1·80618	4024
20	81·9	82·0	1·91381	6256
15	113·85	114·5	2·05881	10990
12	150·0	149·9	2·17580	17103
		188·5	2·27531	24718
8	255·0	252·1	2·40175	39120
7	300·0	302·0	2·48001	50970
6	368·1	373·0	2·57171	68877
5	472·3	475·5	2·67715	96008
4·5	553·7	548·5	2·73918	116230
4·0	654·0	638·0	2·80482	141525
3·5	750·0	759·5	2·88053	176860
3·0	933·6	936·5	2·97151	229420

TABLE VII.

Calculated Pressures on Isothermal Curves, at definite volumes.

Vol.	Temperature.									
	0°.	6°.	13°·1.	21°·5.	31°·1.	32°·5.	35°·5.	48°·1.	64°.	100°.
c. c.	mm.	mm.	mm.	mm.	mm.	mm.	mm.	mm.	mm.	mm.
30	11456	11771	...	...	13088	...	...	13981	14816	16706
25	13448	13832	...	...	15439	...	...	16526	17544	19848
20	16130	16622	...	...	18680	...	..	20074	21378	24330
15	20269	20956	...	...	23830	...	...	25776	27597	31719
12	23719	24719	25783	27043	28482	...	29140	31030	33413	38810
10	26742	27873	29212	30796	32605	...	33433	35809	38806	45592
8	29731	31244	33036	35155	37576	37928	38684	41862	45872	54952
7	31476	33288	35433	37971	40870	41291	42197	46003	50800	61680
6	32973	35190	37843	40973	44553	45073	46193	50893	56820	70250
5	33802	36652	40032	44032	48592	49262	50682	56672	64232	
4·5	33510	36800	40700	45310	50570	51340	52980	59890	68620	
4·0	32645	36475	41005	46365	52495	53385	55295	63335	73485	
3·5	30480	35040	40440	46820	54110	55170	57440	67020		
3·0	26240	31860	38520	46380	55370	56680	59620	71290		

It will be seen that the highest calculated pressure is about 73,500 millim. Andrews gives measurements at much higher pressures; but these are few in number and uncertain, and the correction for the compressibility of air is moreover unknown. Hence it was impossible to make use of them in determining the values of *b*.

On reference to Andrews's paper (Phil. Trans. 1876, p. 435) it will be seen that he compared the relation of increase of pressure to temperature-difference at constant volumes, and came to a conclusion opposed to ours. This is owing to his having made very few observations, and having accidentally chosen those which support his statement. If the coefficients of increase of pressure for unit rise of temperature be calculated by means of Table V., it may be noticed that, although irregular, there is no tendency towards a rise or fall of the coefficient.

Regnault has measured the rise of pressure of gaseous carbonic anhydride at constant volume. He gives the results of four experiments, none of which are available for our purpose, inasmuch as the volumes of a gram are too large.

Reverting to the behaviour of ether, as shown on Plate IV., it will be seen that the curves have been drawn in the region where measurements are impossible. These curves have all the same general form. After rise of pressure and decrease of volume have proceeded for some distance, the curves bend downward, presenting the abnormal feature of decrease of volume with fall of pressure. The pressure continues thus to fall, and at 160° the isothermal touches zero-pressure. At lower temperatures, with small volumes, the pressure becomes negative, and may even represent an enormous tension. At 0° the isothermal at vol. 1·85 cub. centim. per gram reaches the almost incredibly great tension of −271,700 millim.; and it has at that volume (the smallest our results allow us to calculate) by no means reached its limit. At still smaller volumes the tension would doubtless still increase, until the curve turned, and further decrease of volume would be represented, as it is at higher temperatures, by increase of pressure.

The existence of these unrealizable portions of such isothermal curves was, we believe, first suggested by Prof. James Thomson, in a paper in the 'Proceedings of the Belfast Natural History and Philosophical Society,' Nov. 29, 1871. Since that time attempts have been made to express relations between the pressure, temperature, and volume of gases and liquids by Van der Waals and by Clausius; and the formulæ which they propose, and which we hope to consider in a subsequent paper, give isothermals of similar form. Portions of these curves have, indeed, been experimentally verified. In

Professor Thomson's paper, above referred to, he points out that Donny, Dufour, and others have observed the phenomenon commonly alluded to as "boiling with bumping." This is usually the effect of a rise of temperature at constant pressure. But it may equally well be produced, as we have frequently had occasion to remark, at constant temperature by lowering pressure. If the diagram on plate iii. in our memoir on alcohol (Phil. Trans. 1886, part i. p. 156) be referred to, it will be seen that our actual measurement of such reduced pressure was made on the isothermal 181°·4. Mr. John Aitken, in an extended series of experiments on this subject (Trans. Royal Scott. Soc. of Arts, vol. ix.), has shown that such "superheating" can take place only in absence of a free surface, *i. e.* the existence of gaseous nuclei in the liquid, into which evaporation may take place. And Mr. Aitken has also shown that a gas may be compressed to a volume smaller than that at which liquefaction usually occurs, at any given temperature, without formation of liquid. The space, again, if no nuclei be present on which condensation may take place, remains "supersaturated with vapour." It is evidently, therefore, only the instability of such conditions which prevents their complete realization*.

The formulæ of Clausius and Van der Waals are based on the assumption that two causes are in operation (those referred to in the beginning of this paper), viz. the actual size of the molecules, and their mutual attraction. It is possible, by help of these assumptions, to realize the nature of the continuous change from the gaseous to the liquid state of matter. When a gas at a given temperature is reduced in volume its molecules necessarily approach each other, and their attraction for one another increases. This attraction aids the increase of pressure in reducing volume. When a certain volume is reached, the attraction has become so marked that further reduction of volume is accompanied by fall of pressure. If a certain volume be chosen on the descending portion of an isothermal, a state of balance may be imagined where pressure and cohesion unite in maintaining the volume constant against the kinetic energy of the molecules, tending to cause expansion.

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* The reasoning of a recent paper by Wroblewski (*Monatshefte der Chemie*, Wien, July 1886, p. 383) rests on the assumption that such conditions are inconceivable. He supposes lines of equal density to be curves, and on their close approach to the vapour-pressure curve to run parallel with it. His conclusions are therefore not borne out by experimental facts.

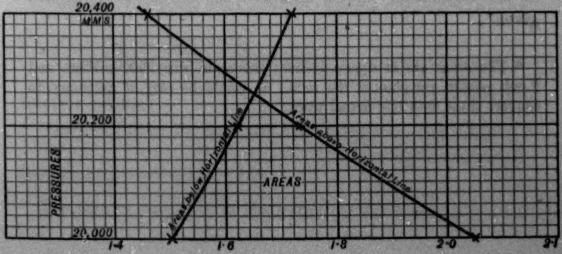
The conception of negative pressure, or tension, is that at low temperatures and small volumes the cohesion is such that, in order to overcome it and increase volume, it would be necessary to apply tension to each molecule. But after the lowest pressure or greatest tension has been attained, the actual size of the molecules presents a bar to closer approach; and to cause further decrease of volume pressure must again be applied. It is not to be supposed that at any given volume only one of these factors is operative; the actual size of the molecules exerts its influence even at large volumes, and the cohesion does not disappear, but no doubt immensely increases, as the volume is reduced, even when that reduction requires rise of pressure. Still, a mental picture of the process may, we think, best be attained by directing attention to cohesion, when volume is being decreased with fall of pressure, and to the influence of the actual size of the molecules when volume is small.

When a liquid is converted into gas, heat is absorbed, or work is done on the liquid. We have previously (*loc. cit.*) given tables showing the heats of vaporization of ether at various temperatures. Our experiments have confirmed the prediction that the heat of vaporization of stable liquids decreases with rise of temperature, and in all probability becomes zero at the critical temperature. Now the volume of a fluid may be changed, either keeping the pressure constant or allowing it to vary during the operation; but if the initial pressure and final pressure are the same, the variation of pressure during the operation does not affect the total work done. A liquid may be changed into saturated vapour at any given temperature in the usual manner, when the intermediate states are represented by non-homogeneous mixtures of liquid and saturated vapour. The area enclosed between the vapour-pressure line and lines drawn vertically from its terminal points, cut by the line of zero pressure (or pressure × change of volume), represents graphically the external work performed in evaporating a liquid. If, however, the change of condition be not abrupt, but continuous, the area enclosed by the isothermal below the vapour-pressure line must be equal to that above the vapour-pressure line (see Plate IV.). If this were not the case, the amount of work required to effect the continuous change would differ from that required for the abrupt change of state.

Now it is evident that a slight alteration in the position of the vapour-pressure line would have great influence on the relative areas enclosed by the isothermal above and below the vapour-pressure line; and it may also be seen that, when these areas are rendered equal by a horizontal line, the position of that horizontal line must represent the true vapour-pressure.

We have determined the position of the horizontal line in the following manner:—

Knowing approximately the position of the vapour-pressure line at a given temperature, three pressures were chosen—the highest above and the lowest below the experimentally determined vapour-pressure; and by means of a planimeter (by Stanley of Holborn) the areas enclosed between each horizontal line and the curves respectively below and above it, formed by the isothermal lines, were measured. To ascertain what position of the horizontal line would render these areas equal, the values of each set of three areas were mapped on sectional paper as abscissæ, the pressures corresponding to the position of the horizontal lines being ordinates. The curves passing through the resulting points cut each other at a point which represents the true pressure and the true area. This method is rendered clearer by inspection of the following figure:—



It is evident that these vapour-pressures depend entirely on measurements represented in the diagram outside the area bounded by the curve representing orthobasic volumes of gas and liquid. It will be seen, on reference to the table on p. 204, that the agreement between these calculated vapour-pressures and those experimentally determined is a very close one, the greatest difference being about 1 per cent. This agreement between experimentally observed vapour-pressures and those depending on the formula $p=bt-a$ is very remarkable, and it is difficult to believe that, if the isochoric lines were curves, such an agreement could exist.

What are usually termed vapour-pressures, then, are those pressures at which horizontal lines drawn through them render the areas enclosed by the isothermal lines below the horizontal lines equal to those above them. But there are other two conditions of matter, each of which has its characteristic pressures. One of these is represented by the highest pressure attainable on any isothermal, or the summit of the curve above the vapour-pressure line; and the other the apex of the curve below the vapour-pressure line. Each temperature chosen has its particular value for each of these conditions; and it is evident that the relations between the temperatures and pressures corresponding to the inferior or reversed apices, as well as those corresponding to the superior apices, would each form a special curve.

The following Table gives the final results of the calculation of vapour-pressures by the method of areas; and, for the sake of comparison, the actually found vapour-pressures are appended. The pressures at the superior and inferior apices of the isothermal curves, and also the enclosed areas, are given*.

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* The areas are in square inches; the scale was 2000 millim. and 2 cub. centim. per gram to the inch. It would be easy, if necessary, to convert these data into actual work.

TABLE VIII.

Temperature.	Vapour-pressures, deduced from areas.	Vapour-pressures, mean of observed.	Pressure, superior apex.	Pressure, inferior apex.	Area above or below vapour-pressure line.
°	millim.	millim.	millim.	millim.	sq. in.
192	26350	26331	26490	26125	0·0425
190	25554	25513	25870	24960	0·1245
185	23703	Old, 23623 New, 23763	24510	21660	0·4550
175	20259	Old, 20189 New, 20271	22100	14060	1·6520
160	15900	15778	19090	− 20	4·710
150	13405	13262	17380	−10400	7·551

The three pressure-curves—which we shall name the "ordinary" vapour-pressure curve, the "superior" vapour-pressure curve, formed by the superior apices of the isothermal lines, and the "inferior" vapour-pressure curve, produced by the lower apices of the isothermal lines—must, it is evident, meet at the critical point; and on mapping them, it was found that this was the case. Points were chosen on these curves at equal intervals of temperature, and the constants for formulæ of the type $\log p = a + b\alpha^t$ were calculated for each. As the pressures on the inferior curve below a certain temperature were negative, it was found convenient to add 30,000 millim. to each, which was subsequently subtracted from the result. The constants for the curves are—

Superior curve :

$$a = 3{\cdot}59797\ ;\ \log b = \bar{1}{\cdot}8343195\ ;\ \log \alpha = 0{\cdot}00257762.$$

Ordinary vapour-pressure :

$$a = 6{\cdot}72909\ ;\ \log b = 0{\cdot}4027232\ ;\ \log \alpha = \bar{1}{\cdot}99876897$$

(*b* is here negative).

Inferior curve :

$$a = 4{\cdot}867404\ ;\ \log b = \bar{1}{\cdot}5913793\ ;\ \log \alpha = \bar{1}{\cdot}98382413$$

(*b* is again negative).

In each case $t = t°$ Cent. $-160°$.

The results are given in the following Table :—

TABLE IX.

Temperature.	Ordinary vapour-pressures.		Superior curve-pressures.		Inferior curve-pressures.	
	Read.	Calculated.	Read.	Calculated.	Read.	Calculated.
°	millim.	millim.	millim.	millim.	millim.	millim.
150	13405	13084	17380	17437	−10400	−10185
160	15900	15900	19090	19090	− 20	− 100
175	20259	20259	22100	22100	+14060	+14060
185	23703	23678	24510	24549	21660	21704
190	25554	25556	25870	25935	24960	24900
192	26350	26341	26490	26523	26125	26065
193	......	26739	......	26826	......	26624
193·83	.....	27075	......	27077	......	27077

With exception of the lowest temperature, the agreement between the read and the calculated pressures is close. The extrapolation amounts to only 3°·83. The agreement is close at 192°, and above that temperature the extrapolation is only 1°·83. It will be seen that at that temperature (193°·83) the pressures coincide. The *apparent* critical point was 193°·8.

Isochoric Lines.

Plate VI. represents the whole of the isochors which we have calculated between the volumes of 1·85 and 300 cub. centim. per gram.

If the gas followed Boyle's and Gay-Lussac's laws absolutely, under all conditions, the isochoric lines would all radiate from zero pressure, and would become more and more vertical as the volumes decreased; and the tangents of the angles formed by these lines with the horizontal line of zero pressure would be proportional to c in the equation $p=ct$, where c varies inversely as the volume. But our equation, $p=bt-a$, introduces another term, a, which is negative. These values of a are represented on the diagram by the extremities of the isochoric lines, where they cut the vertical line representing absolute zero of temperature. The tangents of the angles made by these lines with a horizontal line are proportional to the values of b in our equation.

On referring to Plate VI. it will be noticed that, beginning at the largest volume, two adjacent isochors cut each other at a point, as regards pressure and temperature, not far above zero. With decreasing volumes the points of intersection of adjacent isochors occur at higher and rapidly increasing temperatures and slowly increasing pressures ; and this proceeds until the critical volume is reached. With still smaller volumes, however, the points of intersection of adjacent isochors occur at lower and decreasing temperatures and pressures ; the former decrease slowly, but the latter with great rapidity, and soon extend into the region of negative pressures.

It is evident from the diagram that each isochor between the largest and the critical volume is the tangent of a curve, representing the relations of pressure to temperature ; while the isochors below the critical volume are tangents to another curve, also exhibiting the like relations. Neither of these curves is identical with the vapour-pressure curve, which falls in the area between them.

It will be noticed that, in the area included between the line of zero pressure and these two curves, each isochoric line is cut by two others at every point along its whole length ; but outside this surface, and above the line of zero pressure, no two lines cut each other, and below the line of zero pressure each isochor is cut at each point by one other. The physical meaning of the fact that within the first-mentioned region three isochors intersect each other at one point is, that a gram of the substance may occupy three different volumes at the same temperature and pressure. Now, on referring to the diagram on Plate IV., representing the experimentally unrealizable portions of the isothermal curves, it is evident that on each isothermal line, at pressures limited by the superior or inferior apices of the isothermal, there are, corresponding to each pressure, three volumes. At any pressure above or below these pressures the isothermal line is cut only once, by a horizontal line of equal pressure ; so that, for each pressure, there is only one corresponding volume. At each apex a horizontal line of equal pressure cuts the isothermal line at one point, and is also a tangent to the apex. There are, therefore, two volumes corresponding to each of these pressures. Since no gas can be submitted to a negative pressure, those portions of an isothermal line representing the truly gaseous condition of matter never extend below the horizontal line of zero pressure ; only those portions of the isothermal which proceed towards the inferior apex fall below this line. An isothermal line below zero pressure is therefore cut only twice by a line of equal pressure, and there are therefore two volumes corresponding to each pressure. At each inferior apex, however, the horizontal line is a tangent to the curve, and there is therefore only one volume corresponding to a given pressure.

On referring back to Plate VI., it will be seen that the pressures corresponding to the superior apices of each isothermal line, when mapped, produce the curve AC; and those corresponding to the inferior apices, the curve BC. The surface bounded by these curves and the line of zero pressure corresponds to portions of the isothermal lines, including pressures between the two apices, and each point in the surface is the locus of intersection of three isochoric lines. Below the line of zero pressure the isochoric lines corresponding to the gaseous state are absent; and hence each point is the locus of intersection of only two isochors. The isothermal lines above and below the limits of pressure given by the apices are cut only once by any line of equal pressure; hence the isochors outside the area ACD, and above the line of zero pressure, do not intersect. The apex C of the curvilateral triangle ACD is the point of highest temperature and pressure at which intersection can take place, and therefore represents the critical point; it is also the common point of intersection of the three pressure-temperature curves.

Referring now to Plate V., in which the isochoric lines in the neighbourhood of the critical point are shown on a larger scale, it will be seen that the isochoric lines above a volume not far removed from 4 cub. centim. per gram cut the ordinary vapour-pressure curve CE on one side, while those below the volume 3·75 evidently cut the vapour-pressure line on its other side. There must therefore be an isochoric line which does not cut the curve at all, but forms a tangent to its end-point. That isochor gives the critical volume. It may be determined by calculating the value of $\frac{dp}{dt}$ at the critical temperature. This value of $\frac{dp}{dt}$ is identical with the value of b in our equation $p=bt-a$ at the critical volume.

Until a mathematical expression is discovered, representing b as a function of volume, the only means at our disposal for ascertaining the true volume corresponding to b is by interpolation of the original curve by which the values of b were smoothed. The common point of intersection of the three pressure-temperature curves has been shown on p. 216 to lie at the temperature 193°·83. The value of $\frac{dp}{dt}$ on the vapour-pressure curve at this temperature, calculated by the formula of which the constants have already been given, is 405 millim., which is also the value of b at that temperature. The volume corresponding to this value is 4·06 cub. centim. per gram; and the specific gravity of ether at its critical point is therefore 0·2463.

Unfortunately, Dr. Andrews's measurements of the constants of carbon dioxide are not sufficiently numerous to warrant an attempt to obtain the critical temperature, pressure, and volume by this method. The critical volume of carbon dioxide is evidently less than 3 cub. centim. per gram; but the values of b below that quantity are unascertainable. It may be noticed that the curves below volume 3 are inserted in broken lines, showing a probable course; but no reading from them would be permissible.

The two liquids, ether and carbon dioxide, have no chemical analogy with one another; and we therefore feel justified in concluding that the law which is the subject of this paper is generally applicable to all stable substances. We have, however, other less complete data for methyl and ethyl alcohols, which, so far as they go, are confirmatory of the results described. We have also data available for the examination of acetic acid—a substance which differs from those mentioned, inasmuch as it undergoes dissociation when heated; and we hope shortly to be able to communicate an account of its behaviour.

Professor Fitzgerald, to whom we gave a short account of this law, has recently communicated to the Royal Society a paper in which its thermodynamical bearings are considered.

Bristol, 12th February, 1887.

XXX. *On the Determination of Coefficients of Mutual Induction by means of the Ballistic Galvanometer and Earth-Inductor.* *By* R. H. M. Bosanquet[*].

My attention was drawn to this subject by the paper recently read before the Society by Prof. Foster[†]. I observed at once that the appliances which I am in the habit of using afford a very simple solution of the problem.

The ballistic galvanometer has a resistance less than 2 B.A. units, and about 500 turns. I have three earth induction-coils, all having a mean diameter of about half a metre, and the following constants. The resistances are approximate, as they vary so much with temperature. The wires are all cotton-covered copper.

Number of turns. N.	Total effective area. log NA.	Mean circumference.	Approximate resistance. B.A.	Wire. B.W.G.
42	4·97132	167·325	·6	16
250	5·74200	166·583	10·8	20
1000	6·36182	170·005	42	20

The circular channels are turned in wooden rings framed together in many pieces. They were turned in the Royal Society's lathe in my laboratory. They are mounted so as to turn on vertical axes through half a revolution, in doing which they are reversed with respect to the horizontal component of the earth's magnetism, and so experience an electrical impulse equal to 2 NAH.

If the resistance of the circuit be R, a transfer of electricity then takes place, such that

$$Q_0 = \frac{2\,\text{NAH}}{\text{R}}.$$

The various windings of the coils were measured with great care during the construction. The areas were calculated for each layer separately; and the above values of log NA are probably certain to the fourth place of decimals.

There are two tangent-galvanometers, both on Helmholtz's pattern, having mean circumferences of exactly 1 metre. The one has 2 coils, the other 18. The currents in them are measured by the formula

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[*] Read February 26, 1887.

[†] *Antè*, p. 137.

$$C = GH \tan\theta;$$

where log G has the values:—

No. of coils.	log G.
2	·24797
18	$\bar{1}$·29373

We can now proceed to the problem.

Two coils, P, S, are placed side by side, and a current passed through P; then, on making the contact, a ballistic galvanometer in the circuit of S is deflected. The earth induction-coil forms part of the circuit of S.

So far we have the equations

$$C = GH \tan\theta, \quad \ldots \ldots \quad (1)$$

$$Q = \frac{MC}{R}, \quad \ldots \ldots \quad (2)$$

with reading = α minutes of arc.

If we now give the earth induction-coil a half turn, we have

$$Q_0 = \frac{2NAH}{R}, \quad \ldots \ldots \quad (3)$$

with reading = β minutes of arc.

$$\text{Whence} \quad \frac{Q}{Q_0} = \frac{MG \tan\theta}{2NA}$$

$$= \frac{\alpha}{\beta}$$

by the principle of the ballistic galvanometer. And

$$M = \frac{\alpha}{\beta} \frac{2NA}{G \tan\theta}. \quad \ldots \ldots \quad (4)$$

The 2 disappears from the numerator if the observation is made by reversal.

In order that H may be the same for the tangent-galvanometer and the earth induction-coil, it is necessary to remove the tangent-galvanometer and put the earth induction-coil in its place before making the observation β.

There are two classes of cases which cannot be treated by this most simple form of the method :—

(*a*) Where the quantity of electricity to be dealt with is too large for the galvanometer, even with the coil of highest resistance. And

(*b*) where the resistance of one of the coils to be determined is so great that no earth induction-coil could throw a sufficient quantity of electricity through it.

In both these cases we have to introduce a large resistance into the circuit S, after calibrating the galvanometer without it. The value of the deflection is then altered in the ratio of the change of resistance.

Let R be the total increased resistance,
R_0 the resistance without the addition.

Then equations (2), (3), (4) become

$$Q=\frac{MC}{R}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

$$Q_0=\frac{2NAH}{R_0}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

$$M=\frac{2\alpha RNA}{\beta R_0 G \tan\theta}. \quad . \quad . \quad . \quad . \quad . \quad (7)$$

The 2 disappears, as before, when reversal is employed.

An example of case (*a*) is given later; where, in the second determination of my Gramme machine, a resistance of 1000 B.A. units was introduced into the secondary circuit, to moderate the deflection. The determination of the resistances, however, can hardly ever be accurate, as the copper earth induction-coil is liable to great alterations through change of temperature.

An example of case (*b*) would be afforded by the determination of such an induction-coil as the one by Apps, with high resistance S, mentioned in Prof. Foster's paper. In this case the galvanometer would be calibrated by the earth induction-coil, the high resistance-coil then introduced, and the known values of R, R_0 employed in formula (7).

The determinations I have made are mostly of the mutual coefficients of the coils of my earth-inductors, placed close together. I have also made a couple of determinations of the coefficient of field-magnets and armature in my A Gramme machine.

The determination of February 21 was rather rough; the coils were placed together in their frames, but they could not be brought very near. The numbers are useful, as illustrating the increase of the discrepancy of Maxwell's formula, with the increase of b, the distance of the central planes. In fact, unless b is small compared with the diameters, the formula is not properly applicable. Here it is about half either of the radii, and calculated and observed values are nearly as 4 : 5.

On February 22 the coils were dismounted and brought as close together as possible, b being now between a quarter and a third of either of the radii. The calculated and observed values are nearly as 5 : 6. In order to see what part of the error was due to the dimensions of the section of the coils, the coefficient was then calculated by the more accurate formula referred to below; but the improvement is very slight. It appears that this formula does not in any way cure that defect, which arises from the distance of the central planes. So that in coils similar to mine we cannot expect to get nearer by calculation than the number last referred to, which is to the observed number nearly as 6 : 7.

On February 23 experiments were arranged with a view to test the consistency of the method, the coils examined being made primary and secondary alternately. Though the mode of observation does not admit of great accuracy, it appears that there is a systematic difference between the results of the two arrangements, amounting to about 1½ per cent. This I have not been able to explain. The coefficients of self-induction of the coils should have no influence; but that of the 250 will be very much greater than that of the 42, and this is the only source of error that I can suggest. The number calculated by Maxwell's original formula is to the mean of observation nearly as 6 : 7.

In all the experiments difficulty was experienced in consequence of the continual fall of the battery-current. Without care in charging, and freshly charged cells, the experiments could hardly be made, as the fall of the current affects the galvanometer in the intervals.

Rowland's method of control, with a magnet and coil, was employed.

The determinations of the coefficient of the Gramme machine were very rough. In fact the fundamental equation (2) is not really applicable to the dynamo at all, except perhaps in the upper part of its range, where the current is, say, 10 amperes or more. For small currents do not do more than shake the subpermanent magnetism, which is considerable compared with the magnetism due to small currents. And in motion the machine makes use of this subpermanent magnetism, although it does not enter into the electrical coefficient of mutual induction.

The observations of Feb. 24 were very irregular; it appeared as if the current sometimes shook the subpermanent magnetism and sometimes not. Still a mean was fairly deducible.

On Feb. 25 a stronger current was employed, and the observations were fairly regular; but this current, though it moves the subpermanent magnetism, is quite insufficient to reverse it as the reversal of a large current does; so that even here we do not get a representation of the whole effect.

In the higher part of the range of the machine, say for unit-current (10 amperes), we can assume, without serious error, that the fundamental equation (2) holds. That being so, we can deduce the value of M from the resistance and number of revolutions with which a stable current is produced.

It will be convenient to assume that all the coils of the armature are gathered up into two coils at right angles. Then, if one be parallel and the other perpendicular to the axis of the magnetic field, the determination of the coefficient of induction at rest affects only one of the coils, or half the armature.

Then, as to one of these coils, or half the armature:—In a half revolution the same effect is produced as if the exciting current were reversed, and a quantity of electricity passes,

$$=\frac{2MC}{R}.$$

In a whole revolution $\frac{4MC}{R}$ passes.

The same applies to the other half of the armature, so that altogether $\frac{8MC}{R}$ passes in each revolution.

If there be n revolutions per second, the quantity passing in n revolutions = the current numerically, and this divides out, so that

$$M = \frac{R}{8n}.$$

In an old paper of mine on Practical Electricity (Phil. Mag. xiv. p. 246) I find data from which, by interpolation, I obtain the corresponding values for this machine:—

n' per minute.	R.	C.
840	$10^9 \times 5{\cdot}55$	$1 = 10$ amperes.

Whence $M = 10^7 \times 4{\cdot}95$.

The assumption made above is rough, but we cannot specialize further unless the distribution of the field is known. The two coils may then be supposed to be in any required proportion instead of being equal.

Regarding the coefficient as the product of the number of windings of armature and magnets, and of the magnetic induction common to both, due to unit-current, we can find the common magnetic induction in this case. There are 1700 turns in the armature, half of which count, and 234 turns on each of the four magnets, two of which receive each part of the common induction. Whence the common magnetic induction is

$$\frac{10^7 \times 4{\cdot}95}{468 \times 850} = 125.$$

This seems very small. But the dimensions of the armature are such that it can have hardly any core.

But I must not now pursue the subject of the dynamo.

The method of the earth induction-coil and ballistic galvanometer is susceptible of numerous applications. I have in my mind the direct determination of the capacity of a condenser, and a method following the lines of that used by Weber, for the determination of resistance. He employed earth induction-coils on this principle, though I do not know how they were arranged in detail. I cannot conceive how a tangent galvanometer could be employed for the ballistic work, as seems to be contemplated in Maxwell's account. I should determine the constant of the ballistic galvanometer for the purpose by a shunt comparison with a tangent galvanometer. I believe Mr. Glazebrook has done something of this kind in another case. In fact I have been through the work of such a method; but where there is a shunt to be verified, in this case 1 : 10,000, as well as other determinations of resistances, the errors of temperature are so troublesome to deal with, that in the present state of the subject I doubt whether it is worth while to spend much labour on it.

The numerical results of the experiments referred to are appended.

Coefficients of Induction of 250 *and* 100 *coils.*

Feb. 21. Distance between central planes, $b=13\cdot97$ centims.
β by half turn of 1000 coil.

Arrangement.	α.	β.	θ.	Galvanometer.		M.
250 P 1000 S	152′·5	164′·5	15° 45′	18	make and break	$10^7\times7\cdot6903$

*Calculation by Maxwell's original formula . . . $10^7\times6\cdot164$

Feb. 22. Distance between central planes, $b=7\cdot925$ centim.
β by half turn of 1000 coil.

Arrangement.	α.	β.	θ.	Galvanometer.		M.
250 P 1000 S	203′·7	170′·	12° 33′	18	make and break	$10^8\times1\cdot2593$

*Calculation by Maxwell's original formula . . . $10^8\times1\cdot070$

*Calculation by formula for dimensions of section of coils $10^8\times1\cdot104$

Data for this last formula :—

$n=1000 \qquad n'=250$
$a=27\cdot056 \qquad a'=26\cdot512$
$b=7\cdot925$
$2h=2\cdot18 \qquad 2h'=\cdot562$
$2k=5\cdot45 \qquad 2k'=5\cdot77$

Coefficients of Induction of 42 *and* 250 *coils.*

Distance between central planes, $b=6\cdot35$ centim.
β by half turn of 1000 coil, in S, throughout.

Date.	Set.	Arrangement.	α.	β.	θ.	Galvanometer.	Make & break or reversal.	M.
Feb. 23.	1	42 P 250 S	202′·2	142′	31° 56′	2	m. b.	$10^6\times5\cdot9390$
	2	250 P 42 S	88·2	173	44 20	18	rev.	$\times6\cdot1075$
Feb. 24.	1	......	86·5	175	43 55·5	...	...	$\times6\cdot0030$
	2	......	85·2	175	43 5	...	...	$\times6\cdot0893$
	3	42 P 250 S	190·2	144·7	29 43	2	m. b.	$\times5\cdot9862$

Calculation by Maxwell's original formula . $10^6\times5\cdot275$

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* New edition of Maxwell's 'Electricity and Magnetism,' vol. ii. pp. 314, 320.

Comparison of arrangements :—

		42 P 250 S			250 P 42 S
Feb. 23.	1	$10^6 \times 5{\cdot}9390$	Feb. 23.	2	$10^6 \times 6{\cdot}1075$
„ 24.	3	$\times 5{\cdot}9862$	„ 24.	1	$\times 6{\cdot}0030$
			„ „	2	$\times 6{\cdot}0893$
Mean		$\times 5{\cdot}9626$	Mean		$\times 6{\cdot}0666$

Mean of both arrangements $10^6 \times 6{\cdot}0146$.

Determinations of Coefficient of Induction of Dynamo Field-magnets and Armature. (A Gramme.)

Feb. 24. P field-magnets, with two bichromates and 10 B.A. units.

S armature, ballistic galvanometer, and 1000 coil.

By reversal.

	α.	β.	θ.	Galvano-meter.	Amperes.	M.
Mean value . .	146′	179′	27° 11′	18	·181	$10^7 \times 1\ 858$
Highest value .	176	...	......	...	...	$\times 2{\cdot}239$
Lowest „ .	113	..	......	...	...	$\times 1{\cdot}438$

Feb. 25. P field-magnets, with two bichromates.

S armature, ballistic galvanometer, and 1000 coil, with and without 1000 B.A. units, so that

$R=1045$, $R_0=45$.

By reversal.

α.	β.	θ.	Galvano-meter.	Amperes.	M.
179′·5	179	39° 24′	2	2·54	$10^7 \times 3{\cdot}685$
By formula $M=\dfrac{R}{8n}$				10·0	$10^7 \times 4{\cdot}95$

ADDENDUM.

March 5. *Supplementary Notes.*

1. Calculation of coefficients by the elliptic integral table in the new edition of Maxwell, combined with the formula for approximation to the effect of the sections of the coils.

I have now calculated the experiments of Feb. 22 and Feb. 23–24 by this method, which is the most complete that exists, short of calculating all the single combinations of circles in the two coils. The accordance with experiment is somewhat better, but still far from close.

		Observed.	Calculated.
Feb.	22.	$10^8 \times 1{\cdot}259$	$10^8 \times 1{\cdot}176$
„	23–24.	$10^6 \times 6{\cdot}015$	$10^6 \times 5{\cdot}585$

2. Simple formula for approximate calculation of the coefficient.

Assume that the field in a due to A is everywhere the same as at the centre of a. Then the total lines of force for unit current are

$$\pi a^2 \times \frac{2\pi A^2}{(A^2+b^2)^{\frac{3}{2}}},$$

where b is the distance between the planes of the circles, or, if $\frac{A}{b} = \tan\theta$, this becomes

$$\frac{2\pi^2 a^2 \sin^3\theta}{A},$$

which is simpler to calculate than Maxwell's approximate formula.

The following is the comparison of this formula with observation.

		Observed.	Calculated.
Feb.	21.	$10^7 \times 7{\cdot}690$	$10^7 \times 8{\cdot}991$
„	22.	$10^8 \times 1{\cdot}259$	$10^8 \times 1{\cdot}133$
„	23–24.	$10^6 \times 6{\cdot}015$	$10^6 \times 5{\cdot}036$

3. Course of values of the coefficient of field-magnets and armature of a dynamo.

The numbers stated in the paper may possibly be misleading, as it is not sufficiently explained that the number determined from the motion of the machine, $\left(\frac{R}{8n}\right)$, is not of the same nature as the two results of determinations made at rest, which precede.

The number determined from $\left(\frac{R}{8n}\right)$ is necessarily infinite when the current is evanescent, if there is any retention of magnetism in the machine, and diminishes continually as the current increases. The following corresponding values of this coefficient and current are given by the data referred to in the paper.

Coefficient.	Current in amperes.
$10^7 \times 7{\cdot}054$	3·8
$\times 6{\cdot}250$	5·5
$\times 5{\cdot}600$	7·6
$\times 4{\cdot}732$	10·5

XXXI. *On Delicate Thermometers.* *By* Spencer Umfreville Pickering, *M.A., Professor of Chemistry at Bedford College*[*].

Some months ago I had the honour of bringing before the notice of this Society (*antè*, p. 8) the fact that with very delicate thermometers the temperature registered was never exactly the same when the column had risen to the point of rest as when it had fallen to it. The investigation was made by placing the instrument in a large calorimeter of water, removing the bulb at intervals, cooling or heating it slightly, and then replacing it and observing the reading. About eight separate observations were made in order to determine the difference between the falling and rising readings at any particular point on the stem; and throughout the observations the instrument was tapped continuously on the upper end [†] to overcome the inertia of the mercury in the tube. The difference which was noticed was explained at the time by the bulb not being of precisely the same shape while the mercury was being forced upwards through the fine tube as when it was being dragged downwards; nevertheless there were several points which rendered such an explanation not altogether satisfactory. One out of the two instruments examined (No. 62839) gave differences proportional to the height of the column in the tube; in the other (No. 63616) no such proportionality was noticed: moreover, the instrument which showed this defect to the greatest extent (63616) was the one which had the smallest and strongest bulb. I was subsequently indebted to Lord Rayleigh for a suggestion that these differences should be attributed to the capillarity of the tubes acting on the expansibility of the bulbs, and not to the action of the bulbs only, and thus the differences observed between the behaviour of the two instruments might easily be accounted for by slight differences in the shape or size of the bore at various points. In order to test the validity of such an explanation, which at first sight appeared highly probable, other experiments were performed with these instruments, taking care to make all the observations at exactly the same temperature, removing some of the mercury into the upper chamber, so as to make the different points on the scale correspond to the same Centigrade temperature. The somewhat bulky details of the experiments may here be omitted, and the general results only given. Table I. contains these results; those which were obtained originally, and have been given in the previous communication, are marked by an asterisk; and any small discrepancies observed between them and the fresh experiments may be attributed to differences in the actual temperature of the observations, the recent experiments only being strictly comparable with each other, having all been performed at $10^{\text{c}}{\cdot}5$ C. The readings and the differences are expressed here in mm. of the column, instead of cm. (or scale-degrees) as in the former communication.

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[*] Read April 23, 1887.

[†] I now employ a clockwork tapping apparatus for this purpose.

Table I.

Thermometer No. '39.

Scale-Reading	465	457*	270*	162	142* mm.
Difference in falling and rising readings.	0·5	·46*	·27*	·17	·15* mm.
Relative capacity of tube at the point taken	46·1	46·1	45	45·6	45·6

Thermometer No. '616.

Scale-Reading	562	458	458*	289	154	142	140* mm.
Difference in falling and rising readings.	0·73	·42	·96*	·78	·67	·62	·91* mm.
Relative capacity of tube at the point taken	40·3	40	40	39·3	40·1	40·1	40·1

To whichever thermometer we confine our attention, it is perfectly obvious that the magnitude of the differences bears no relation to the size of the bore. Taking the original experiments with '39, the difference as judged by the size of the bore should be least at 457, and greatest at 270, and of intermediate value at 142 mm.; whereas they are found to be greatest at 457 and least at 142 mm. Again, with No. '616, the differences should be greatest at 289, and least at 562 mm.; whereas they are practically equal at these two points, and greater (taking the later experiments only) than at any other points. It may be objected, however, that the capacity of the tube at these points, as given by the length of a comparatively long (2 cm.) thread of mercury in that position, affords but a very rough, and perhaps quite erroneous, measure of the diameter of the tube at the particular point in question. As a crucial test, therefore, it was determined to alter the bulb of one of the instruments. This was done with Thermometer '39. The capacity of the bulb was reduced to half its former value, so as to hold 18 instead of 36 grams of mercury; and a determination of the coefficients of expansion of the two bulbs under pressure (given in column 6 of Table II.) shows that what may be termed the apparent expansion, or the effect of pressure on the height of the mercury in the tube, was thereby reduced to nearly half its former value, from ·042 to ·025 mm. per mm. of mercury-pressure, so that the differences in the readings with falling and rising columns should have been diminished in that proportion, if it depended on the expansion of the bulb by pressure; but on examination it was found that this difference was even greater now than it had been previously—at 270 mm. it amounted to ·59 instead of ·27 mm., and at 457 mm. it was ·39 instead of ·46 mm. (col. 7 of Table II.). Another thermometer (No. '83) was then examined in a similar manner. Originally it exhibited no difference whatever in the falling and rising readings; but when the bulb was altered, without increasing the coefficient of apparent expansion to any considerable extent (from ·011 to ·015), a small though unmistakable difference in the readings was observed (No. '83 B in the table). This second bulb was then removed, and a third and smaller one substituted for it (No. '83 C), by which the coefficient of apparent expansion was reduced by one half its former value; but, instead of the differences being diminished, they were actually increased, although no accurate measure could be made of them, for the column of mercury in the tube kept breaking off when the instrument was tapped. It was evident, therefore, that the cause of these differences in the readings did not lie in the bulbs of the instruments, but in the stems, that each time the instrument was opened and air admitted into the stem, the defect was increased, till the tube eventually became entirely ruined. The moisture and gases present in the air, no doubt, affect the glass and adhere so strongly to it that the heating to which the stem is sub-

Table II.

Instrument.	Mercury in bulb.	Relative capacity of tube.	Value of 1 mm. of column.	Coeff. of expansion of bulb per mm. mercury-pressure.	Alteration in height of column per mm. mercury pressure.	Difference of readings with falling and rising column.	Description of bulb.
					mm.		
'616.	30·5 grams	40	0°·0064 C.	0·000,000,034,8	0·0303	0·42 to 0·78 mm.	Double, glass cylinder.
'39.	36·2 grams	45	0·006 C.	0·000,000,045,8	0·0424	0·15 to 0·45 mm.	Single, glass cylinder.
'39 B.	18·1 grams	45	0·012 C.	0·000,000,054,3	0·0252	0·39 to 0·59 mm.	Single, blown.
'83.	15·6 grams	100	0·038 C.	0·000,000,064,6	0·0114	Nil.	Single, blown.
'83 B.	28·5 grams	100	0·027 C.	0·000,000,041,5	0·0147	0·04 to 0·32 mm.	Single, glass cylinder.
'83 C.	19·4 grams	100	0·0304 C.	0·000,000,03	0·0075	Large.	Single, glass cylinder.
'08.	38·8 grams	76	0·0116 C.	0·000,000,030,1	0·0145	Nil.	Double, glass cylinder.
'61.	46·0 grams	72	0·0097 C.	0·000,000,033,2	0·0191	Nil.	Double, glass cylinder.
'16.	15·4 grams	100	0·0385 C.	0·000,000,035,6	0·0062	Nil.	Single, glass cylinder.

jected is quite incapable of removing it, and the interior of the tube remains coated with an elastic covering which destroys the working capabilities of the instrument. The researches of Bottomley (Proc. Roy. Soc. xxxviii. p. 158) and others on the absorption of air, and especially carbon dioxide, by glass, prove, in a striking manner, the extent to which such absorption occurs, and the persistence with which the absorbed gases are retained.

Both the delicate instruments ('39 and '616), in which the difference of the readings was first observed, had had small temporary bulbs attached for the purpose of calibration; and it therefore seemed probable that the second opening of the tube may have been the sole cause of the defects which they exhibited. To settle this question, and to ascertain whether it was possible to make instruments of such delicacy entirely free from this defect, two other thermometers were manufactured, Nos '08 and '61. The delicacy of these was somewhat less than in the former instruments, owing to the impossibility of procuring sufficiently fine tubes; the size of the bulbs, however, was increased, that of '61 containing as much as 46 grams of mercury. An estimation-figure, ·05 mm., represented about 0·0005°C. On examining these instruments, in the same manner as previously, it was found that they worked perfectly, the mercury registering exactly the same temperature whether the column had risen or fallen to the point of rest, equally satisfactory results being obtained whatever portion of the stem was examined. Instruments of this excessive delicacy are therefore perfectly workable; it is, however, only by observing the utmost precaution in making them that success can be obtained. The tube must on no account be opened till the last minute, when the bulb is finished and ready to be attached without a moment's delay; the bulb, as soon as it is attached, must be warmed so as to fill the tube with mercury and prevent the access of air through the upper end. If any failure occurs in the attachment of the bulb at the first trial, the stem must be rejected; a second attempt would be attended with the same results as putting on a second bulb after the instrument had been made up. When once the stem is filled with mercury, the tube may apparently be opened several times at the top without damage being done, and the bulb itself may be made 24 hours before it is attached to the stem without being injured by exposure to air for that time.

It is a common practice of thermometer-makers to examine the bore of a tube before it is made into a thermometer by passing a thread of mercury along it, and often, indeed, the stems are divided and fully calibrated before the bulb is attached and the tube closed. From what has been ascertained as to the effect of the air on the interior of the tube, it is obvious that a tube which has been treated in such a manner will be utterly useless for any really delicate instrument.

XXXII. *On the Effect of Pressure on Thermometer-bulbs, and on some Sources of Error in Thermometers.* *By* SPENCER UMFREVILLE PICKERING, *M.A.*, *Professor of Chemistry at Bedford College*[*].

THE great difficulty which exists in obtaining exact concordance between two thermometers throughout a considerable range of their scales must have been experienced by all who have had occasion to require such concordance. In the course of a series of experiments, in which the temperature-disturbance in a calorimeter was measured simultaneously with two instruments, I was much struck by the appearance of a certain amount of regularity in the difference in the results yielded by the two instruments, which, according to direct comparisons with each other through longer ranges of temperature, should have been absolutely concordant. The instruments being open in the scale and having large bulbs, I was led to seek for an explanation of these discrepancies in irregularities in the expansion of the bulbs under the pressure of the column of mercury in the tube.

The effect of pressure on a thermometer-bulb has been investigated by Egen (Pogg. *Ann.* xi. p. 283), and by Mills (Roy. Soc. Edin. xxix. p. 285), with the general result of showing that the expansion experienced is directly proportional to the pressure. But although the pressures employed

[*] Read April 23, 1887.

in Mills's experiments were considerable (ranging up to 134 atmospheres), the thermometers which he examined were not of the most delicate character, and the coefficient of expansion was but small in comparison with that possessed by most calorimetric instruments. In the present experiments the bulb of the thermometer was enclosed in a small thin brass cylinder, which was connected with a pump, by means of which a vacuum, or pressure up to two atmospheres, might be produced. The case enclosing the bulb was previously filled with melting ice and placed in a large vessel of the same, the zero point of the thermometer having been previously adjusted so as to be slightly above the level of the ice.

Three instruments were investigated in this manner, Nos. 62839, 63616, and 65108, of which the details of construction are given in the table ii. of the preceding communication (see also *antè*, pp. 9, 19). About twenty observations at different pressures were made in each case, and the results are given in Table I., where are entered the observed pressures and readings in millim., and also the readings, calculated on the assumption that the alteration in height of the column is directly proportional to the pressure; these calculated values being deduced from the average points given at the foot of the table. With the last-mentioned instrument (65108) the effect of pressure on the bulb would appear to cause a very regular expansion; there are only three observations which differ from the calculated values by more than 0·1 millim., while the average difference amounts to about 0·05 millim. only. With the other two instruments the observations at the higher pressures cannot be much relied on, since the pressures were ascertained by means of a Bourdon's gauge, instead of a column of mercury as in the other cases; and this gauge was afterwards found to be untrustworthy. Omitting these observations, we find that, in case of No. 63616, where the coefficient of apparent expansion of the bulb was twice as great as that of 65108, the error in the readings is considerably larger, amounting to as much as 0·12 millim. on the average, while the grouping together of the positive and negative differences is well marked. It is only with No. 62839, however, which possessed a still greater coefficient of expansion, that the differences become so large

TABLE I.—Effect of Pressure on the Bulbs of Thermometers.

Thermometer 62839.			
External pressure in mm. of mercury.	Observed reading.	Calculated reading.	Difference.
	mm.	mm.	mm.
1986	97·80	99·40	−1·60
1718	86·60	89·00	−2·40
1438	75·35	77·15	−1·80
1254	68·70	69·35	−0·65
1093	62·65	62·50	+0·15
928	56·25	55·50	+0·75
851	52·85	52·25	+0·60
723	48·00	46·80	+1·20
665	45·55	44·35	+1·20
596	42·55	41·45	+1·10
516	38·15	38·05	+0·10
416	33·80	33·80	0
316	29·45	29·55	−0·10
216	25·50	25·30	+0·20
173	23·55	23·50	+0·05
118	21·20	21·15	+0·05
82	19·55	19·60	−0·05
47	18·15	18·15	0
11	16·55	16·60	−0·05
−22·5	15·10	15·20	−0·10
−55	14·00	13·80	+0·20
Average points, 92·5 mm. at 1800 P, and 16·68 mm. at 12·5 P.			

Thermometer 63616.			
External pressure in mm. of mercury.	Observed reading.	Calculated reading.	Difference.
	mm.	mm.	mm.
1960	94·00	94·80	−0·80
1738	87·60	88·10	−0·50
1433	78·75	78·80	−0·05
1180	71·45	71·05	+0·40
1009	66·05	66·00	+0·05
874	61·65	61·85	−0·20
724	57·25	57·30	−0·05
667	55·85	55·60	+0·25
596	53·60	53·45	+0·15
515	51·25	51·00	+0·25
414	48·05	47·90	+0·15
320	44·95	45·05	−0·10
216	41·90	42·00	−0·10
163	40·25	40·30	−0·05
117	38·65	38·90	−0·25
63	37·40	37·35	+0·05
16	35·90	35·85	+0·05
−25	34·60	34·60	0
−56	33·80	33·65	+0·15
Average points, 67·03 mm. at 1044 P, and 36·07 mm. at 23·6 P.			

Thermometer 65108.			
External pressure in mm. of mercury.	Observed reading.	Calculated reading.	Difference.
	mm.	mm.	mm.
1771	43·00	42·95	+0·05
1738	42·45	42·50	−0·05
1660	41·35	41·35	0
1597	40·40	40·45	−0·05
1521·5	39·35	39·35	0
1435	38·15	38·10	+0·05
1328	36·55	36·45	+0·10
1228	35·15	35·10	+0·05
1131·5	33·65	33·70	−0·05
1052	32·25	32·55	−0·30
932	30·85	30·80	+0·05
832·5	29·35	29·35	0
734·5	28·00	28·00	0
634	26·40	26·50	−0·10
519·5	24·80	24·85	−0·05
418·5	23·45	23·40	+0·05
323	22·15	22·00	+0·15
221·5	20·60	20·50	+0·10
125·5	19·15	19·15	0
26	17·75	17·70	+0·05
− 14·5	16·90	17·10	−0·20
− 70·5	16·40	16·30	+0·10
−109	15·75	15·75	0
Average points, 41·32 mm. at 1657·5 P, and 17·20 mm. at −8·5 P.			

as to render it quite impossible to attribute them to mere experimental error. As the pressure is increased above 500 millim., the bulb begins to contract far more than it should, causing a difference of as much as 1·2 millim. between the observed and calculated readings; it then contracts less, crosses the line representing the calculated values and for pressures from 1100 up to 1986 millim. (if these higher results may be trusted) does not contract as much as it should do*. The action of the bulb under pressure is evidently not regular.

As the differences in the calorimetric results above mentioned were observed with the thermometers '616 and '08, which behaved normally, or nearly so, under pressure, as well as with other instruments with bulbs of considerably smaller expansibility, it is impossible to attribute these differences to the cause suggested; at the same time, however, the present investigation leads to results of considerable practical importance. It is evident that where the coefficient of expansion of the bulb is large, as with '39, irregularities in expansion sufficient to introduce considerable errors may occur; the bulb, when subjected to pressure, would appear to behave in a manner analogous to that often noticed with thin tin plate vessels, where a small addition or removal of pressure will cause a sudden and considerable alteration in the form of the vessel. It would certainly be advisable, in the case of any thermometer required for very delicate work, to examine it under pressure to ascertain whether its action be uniform or not. In order to reduce the chances of irregular action, it is necessary to render the bulb as inexpansible as possible. From the fact that the thermometer 63616 showed a slight amount of irregularity in its action, we may place the limits of expansibility desirable in a very fine instrument at a number between that of this instrument and that of 65108; the coefficient of expansion should not exceed 0·000,000,03, or the apparent expansion 0·02 millim. of the mercurial column per millim. of pressure.

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* Care was of course taken that the thermometer should not be read till the column had attained a position of equilibrium. The top of the instrument was tapped throughout the experiments by means of the tapping apparatus, and the column read at intervals of one minute till it was found to be perfectly stationary.

An examination of table ii. of the preceding communication will show at once the increase of rigidity obtained by having the bulb made out of a glass cylinder instead of being blown before the lamp; the instruments '83 and '39 B are the only ones mentioned in this table which had blown bulbs, and the coefficients of expansion in their cases are higher than in any other case, although their bulbs were only ½ and ⅓ as big as those of most of the other instruments. Again, the thermometers '83 and '16 were identical in all respects except as regards their bulbs, and here the blown bulb ('83) possesses only half the strength of that made out of cylinder.

Although it seems probable, *prima facie,* that a blown bulb, however well constructed, would not be so uniform as a cylinder bulb, these facts of course do not prove that such is necessarily the case, as the thickness of the walls of the bulbs was not known; but it does prove that, by ordering a thermometer with a cylinder bulb, we should in all probability get an instrument possessing nearly twice the strength of one with a blown bulb. A further very considerable addition of strength may be gained by having the bulb made double instead of single. The instruments Nos. '616, '08, and '61 possessed double bulbs made out of glass cylinder; and a comparison of them with '83 B and '39, which had single bulbs made out of cylinder also, will show the advantages of the double bulb. For thermometers to be used in a liquid which is stirred in a thoroughly efficient manner, the thickness of the walls of the tube forming the bulb may be very considerable. The instruments Nos. '08 and '61, which contain between 40 and 50 grams of mercury, will take the temperature of the liquid in the calorimeter in about 5 seconds, although their bulbs are 0·75 millim. thick in the walls.

Although the effect of different pressures on the bulb did not appear to produce irregularities such as would account for all the difficulties experienced in getting two instruments to correspond perfectly throughout their scales, it was thought possible that the expansibility of the bulbs under pressure might be influenced to a considerable extent by the temperature of the experiment, and that this might produce discordance between two instruments which had been compared with the same standard but at different temperatures. To investigate this, the behaviour of No. '08 under pressure was examined at 12° C. As it was impossible to keep the temperature of the bath absolutely constant throughout the series of experiments, the reading at any pressure P_1 was compared with that at P by taking the mean of two observations at P, made immediately before and immediately after the observation at P_1. In the following Table the value of the constant obtained from $\frac{R_1-R}{P_1-P}$ (R_1 and R being the readings at P_1 and P respectively) is given in the second column, while P_1-P is given in the first column. P was in all cases the atmospheric pressure. The mean value of the constant (the coefficient of apparent expansion) is 0·0145, a number absolutely identical with that found at 0° (table ii., preceding paper), which shows that small alterations of temperature, such as would occur in standardizing delicate calorimetric thermometers, produce no appreciable alteration in the rigidity of the bulbs. The causes producing non-concordance of thermometers under certain circumstances still remains to be discovered*.

Thermometer '08. Under pressure at 12°.

P_1-P.	$\frac{R_1-R}{P_1-P}$
millim.	
−500	0·01445
−400	0·01445
−300	0·01434
−200	0·01380
+200	0·01470
,,	0·01469
+300	0·01438
,,	0·01462
+400	0·01447
+500	0·01455
+600	0·01457
Mean	0·01453

I may mention one source of error in thermometric work

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[*] For an unexplained instance of non-accordance of results obtained with different thermometers, and also with different portions of the stem of the same thermometer, see Chem. Soc. Trans. 1887, pp. 304, 322.

which attains considerable dimensions when dealing with tubes of very fine bore. These tubes, even when of the most perfect description obtainable, generally possess a few points at which the mercury column experiences a difficulty in passing: the mercury, when it has reached such a point, sticks there an appreciable time, and then passes it suddenly with a jerk; sometimes, even, the mercury sticks so persistently that the column will separate sooner than pass it. These points do not indicate any contraction which is sufficient to affect the results of calibration, and are probably due to some difference in the nature of the glass, for they may be developed by heating the thermometer-tube externally with a very small flame up to about 400°. The error of taking a reading while the mercury is sticking at such a point may, I estimate, amount sometimes to as much as 0·5 millim. All delicate thermometers should be carefully examined in order to ascertain the position of such points, and they should be avoided, if possible, in any work with the instrument.

In any thermochemical work in which the effect of temperature on a given reaction is being studied, many of the sources of error inherent in the use of thermometers may be avoided by using the same portion of the stem of the instrument, whatever the actual temperature may be. To effect this, the zero-point is altered in each experiment by removing some of the mercury into the upper chamber of the thermometer. Formerly I removed the requisite amount of mercury by the application of a very small flame to a point just below this chamber; but I now adopt a method which is much safer, more expeditious, and equally exact. A fine tube, somewhat wider than the stem of the thermometer, is affixed to the upper end of the stem, and in this tube there is a small contraction or "knife-edge," sufficiently wide to permit of the mercury passing it either upwards or downwards, but yet so narrow that a slight swing of the instrument will cause the column of mercury to break off at it, that portion of the mercury which is above the knife-edge passing up into the upper chamber. By this means any point on the stem may be adjusted with ease to within 0°·02 of any given temperature.

INDEX.

A.

Page

Abercromby, Hon. R., on the peculiar sunrise-shadows of Adam's Peak in Ceylon 101
Account of Cauchy's theory of reflection and refraction of light 146
Ackroyd, William, and Emmott, Walter, on an electric-light firedamp indicator 69
Adam's Peak in Ceylon, the peculiar sunrise-shadows of 101
Amalgamation, on the expansion produced by 88
Arc-lamp suitable to be used with the Duboscq lantern 184
Ayrton, W. E., and Perry, John, on the expansion of mercury between 0° C. and $-39°$ C. 86
——, ——, on the expansion produced by amalgamation.......... 88

B.

Baily, Walter, on a map of the world on Flamsteed's projection 32
——, on a theorem relating to curved diffraction-gratings 53
Ballistic galvanometer and earth-inductor 220
Bidwell, Shelford, on a modification of Wheatstone's rheostat...... 50
Bosanquet, R. H. M., on the determination of coefficients of mutual induction by means of the ballistic galvanometer and earth-inductor 220

C.

Calorimetric thermometers, on delicate 8
—— work, experimental error in 1
Cauchy's theory of reflection and refraction of light, an account of.. 146
Cause of the solar diurnal variations of terrestrial magnetism...... 38
Certain sources of error in connection with experiments on torsional vibrations 90
Change of condition from the liquid to the solid state on vapour pressure, influence of 119

Page

Coefficients of mutual induction by means of the ballistic galvanometer and earth-inductor 220
—— of mutual induction, note on a method of determining........ 137
Cornu, M. A., on the distinction between spectral lines of solar and terrestrial origin 95
Critical mean curvature of liquid surfaces of revolution........ 108
—— temperatures of bodies and their thermal expansions as liquids, relation between the 34
Cunynghame, H., on a new hyperbolograph 67
Curvature of liquid surfaces of revolution, on the critical mean 108
Curved diffraction-gratings, on a theorem relating to........ 53

D.

Delicate calorimetric thermometers 8
—— thermometers, on 229
Determination of coefficients of mutual induction by means of the ballistic galvanometer and earth-inductor 220
Determining coefficients of mutual induction, note on a method of.. 137
Distinction between spectral lines of solar and terrestrial origin, on the........ 95
Duboscq lantern, on an arc-lamp suitable to be used with the...... 184

E.

Earth-inductor and ballistic galvanometer 220
Effect of pressure on thermometer-bulbs, and on some sources of error in thermometers 234
Effects on some of the physical properties of iron, the permanent and temporary, produced by raising the temperature to 100° C. 176
Elasticity of iron, the longitudinal and torsional 171
Electric-light fire-damp indicator 69
Electromagnet, further notes on the formulæ of the, and the equations of the dynamo........ 76
Emmott, Walter, and Ackroyd, William, on an electric-light fire-damp indicator........ 69
Equations of the dynamo, further notes on the formulæ of the electromagnet and the........ 76
Error in calorimetric work, on an experimental 1
—— in thermometers, on some sources of 234
Evaporation and dissociation 194
Expansion of mercury between 0° C. and −39° C., on the 86
—— produced by amalgamation, on the 88
Experimental error in calorimetric work 1
Experiments on torsional vibrations, on certain sources of error in connection with 90

F.

Page

Fire-damp indicator, on an electric-light 69

Formulæ of the electromagnet and the equations of the dynamo, further notes on the 76

Foster, G. C., on a method of determining coefficients of mutual induction 137

Further notes on the formulæ of the electromagnet and the equations of the dynamo 76

G.

Gibson, E., and Gregory, R. A., note on the tenacity of spun glass.. 191

Glass, note on the tenacity of spun 191

Gregory, R. A., and Gibson, E., note on the tenacity of spun glass.. 191

H.

Hell-gate explosion, objects connected with the 71

Hyperbolograph, on a new 67

I.

Influence of change of condition from the liquid to the solid state on vapour-pressure 119

Instruments, measuring, used in mechanical testing 179

Iron, on some of the physical properties of 171

——, the internal friction of 172

——, the longitudinal and torsional elasticity of 176

——, the velocity of sound in 177

L.

Lamp, arc-, suitable to be used with the Dubsocq lantern 184

Light, an account of Cauchy's theory of reflection and refraction of 146

Liquid surfaces of revolution, on the critical mean curvature of 108

Longitudinal and torsional elasticity of iron 176

M.

Map of the world on Flamsteed's projection 32

Measuring-instruments used in mechanical testing 179

Mercury, on the expansion of, between 0° C. and −39° C. 86

Method of determinating coefficients of mutual induction, note on a 137

Mode of maintaining tuning-forks by electricity, note on a 72

Modification of Wheatstone's rheostat, on a 50

Mutual induction by means of the ballistic galvanometer and earth-inductor, on the determination of coefficients of 220

N.

Page
Nature of liquids, on the, as shown by a study of the thermal properties of stable and dissociable bodies 127
New hyperbolograph, on a 67
Note on a method of determining coefficients of mutual induction .. 137
—— on a mode of maintaining tuning-forks by electricity 72
—— on a relation between the critical temperatures of bodies and their thermal expansions as liquids 34
—— on the tenacity of spun glass 191

O.

Objects connected with the Hell-gate explosion 71

P.

Permanent and temporary effects on some of the physical properties of iron, produced by raising the temperature to 100° C. 171
Perry, John, and Ayrton, W. E., on the expansion of mercury between 0° C. and – 39° C. 86
——, ——, on the expansion produced by amalgamation 88
Pickering, S. U., on an experimental error in calorimetric work 1
——, on delicate calorimetric thermometers 8
——, on delicate thermometers 229
——, on the effect of pressure on thermometer-bulbs, and on some sources of error in thermometers 234
Pressure, temperature, and volume in saturated vapours, on the relations of 22
Properties of stable and dissociable bodies, and the nature of liquids, as shown by a study of the thermal 127

R.

Ramsay, W., and Young, S., on evaporation and dissociation 194
——, ——, on some thermodynamical relations 56, 61
——, ——, on the influence of change of condition from the liquid to the solid state on vapour-pressure 119
——, ——, on the nature of liquids, as shown by a study of the thermal properties of stable and dissociable bodies 127
Reflection and refraction of light, an account of Cauchy's theory of 146
Relations of pressure, temperature, and volume in saturated vapours 22
Rücker, A. W., on the critical mean curvature of liquid surfaces of revolution 108
——, and Thorpe, T. E., note on a relation between the critical temperature of bodies and their thermal expansions as liquids .. 34

S.

Saturated vapours, the relations of pressure, temperature, and volume in 22

Page
Solar-diurnal variations of terrestrial magnetism, on the cause of the 38
Solid state on vapour-pressure, influence of change of condition from the liquid to the 119
Sound in iron, the velocity of........ 177
Sources of error in connection with experiments on torsional vibrations, on certain 90
—— of error in thermometers, on some 234
Spectral lines of solar and terrestrial origin, on the distinction between........ 95
Sprengel, H., on objects connected with the Hell-gate explosion near New York........ 71
Spun glass, note on the tenacity of 191
Stewart, Balfour, on the cause of the solar-diurnal variations of terrestrial magnetism 38
Study of the thermal properties of stable and dissociable bodies 127
Sunrise-shadows of Adam's Peak in Ceylon, the peculiar........ 101

T.

Tenacity of spun glass, note on the 191
Terrestrial magnetism, on the cause of the solar-diurnal variations of 38
Theorem relating to curved diffraction-gratings, on a 53
Theory of reflection and refraction of light, an account of Cauchy's 146
Thermal properties of stable and dissociable bodies, and the nature of liquids 127
Thermodynamical relations, on some 56, 61
Thermometer-bulbs, on the effect of pressure on 234
Thermometers, on delicate........ 229
——, on delicate calorimetric........ 8
——, on some sources of error in 234
Thompson, S. P., further notes on the formulæ of the electromagnet and the equations of the dynamo 76
——, note on a mode of maintaining tuning-forks by electricity 72
——, on an arc-lamp suitable to be used with the Duboscq lantern 184
Thorpe, T. E., and Rücker, A. W., note on a relation between the critical temperatures of bodies and their thermal expansions as liquids 34
Tomlinson, Herbert, on certain sources of error in connection with experiments on torsional vibrations 90
——, on the permanent and temporary effects on some of the physical properties of iron, produced by raising the temperature to 100° C. 171
Torsional vibrations, on certain sources of error in connection with experiments on........ 90
Tuning-forks, mode of maintaining, by electricity 72

U.

Page

Unwin, W. C., on measuring-instruments used in mechanical testing 179
——, on the relations of pressure, temperature, and volume in saturated vapours 22

V.

Vapour-pressure, influence of change of condition from the liquid to the solid state on 119
Variations of terrestrial magnetism, on the cause of the solar-diurnal 38
Velocity of sound in iron 177

W.

Walker, J., an account of Cauchy's theory of reflection and refraction of light 146
Wheatstone's rheostat, on a modification of 50
World, map of the, on Flamsteed's projection 32

Y.

Young, S., and Ramsay, W., on evaporation and dissociation 194
——, ——, on some thermodynamical relations 56, 61
——, ——, on the influence of change of condition from the liquid to the solid state on vapour-pressure 119
——, ——, on the nature of liquids, as shown by a study of the thermal properties of stable and dissociable bodies 127

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157

PROCEEDINGS

AT THE

MEETINGS OF THE PHYSICAL SOCIETY

OF LONDON.

SESSION 1886-87.

February 13th, 1886.

Dr. F. Guthrie, Vice-President, in the Chair.

The following were elected Members of the Society:—

Prof. T. H. Huxley, F.R.S.; Mr. A. E. Mills.

The following communications were made:—

"On Experimental Errors in Calorimetrical Work, and on Delicate Calorimetrical Thermometers." By Prof. S. U. Pickering.

"On a new Calorimeter." By Prof. W. F. Barrett.

"On a form of Calorimeter." By Prof. S. P. Thompson.

February 27th, 1886.

Dr. Gladstone, Vice-President, in the Chair.

The following were elected Members of the Society:—

Mr. D. E. Jones; Dr. Sydney Young.

The following communications were made :—

"Notes on the Thermodynamic Relations in the Paper of Messrs. Ramsay and Young." By Prof. W. C. UNWIN.

"On a Map of the World in which the proportion of areas is retained." By Mr. WALTER BAILY.

"On a Delicate Calorimetric Thermometer." By Prof. S. U. PICKERING.

March 13th, 1886.

Prof. BALFOUR STEWART, President, in the Chair.

The following were elected Members of the Society :—

A. C. CURTIS-HAYWARD, M.A.; Prof. S. U. PICKERING.

The following communications were made :—

"On the Growth of Filiform Silver." By Dr. J. H. GLADSTONE.

"On Apparatus for measuring the Electrical Resistance of Liquids." By Prof. A. W. REINOLD.

"On Chromatic Photometry." By Capt. ABNEY and Major-Gen. FESTING.

March 27th, 1886.

Prof. W. G. ADAMS, Vice-President, in the Chair.

The following was elected a Member of the Society :—

Mr. A. R. WRIGHT.

The following communications were made :—

"On an Arc Lamp convenient for use with the Duboscq Lantern for projection." By Prof. S. P. THOMPSON.

"On a modified Maxwell's Galvanometer suitable for Lecture-purposes." By Prof. S. P. THOMPSON.

"On the Expansion of Mercury from its Melting-point to Zero Centigrade." By Profs. AYRTON and PERRY.

"On the Deformation of a Straight Bar of Brass produced by amalgamating one edge." By Profs. AYRTON and PERRY.

April 10th, 1886.

Prof. BALFOUR STEWART, President, and afterwards Prof. W. G. ADAMS, Vice-President, in the Chair.

The following communications were made:—

"On the Cause of the Solar-Diurnal Variations of Terrestrial Magnetism." By Prof. BALFOUR STEWART.

"On a Relation between the Critical Temperatures of Bodies and their Thermal Expansions as Liquids." By Prof. A. W. RÜCKER and Prof. T. E. THORPE.

May 8th, 1886.

Prof. H. M'LEOD, Vice-President, in the Chair.

The following was elected a Member of the Society:—

W. A. PRICE, M.A.

The following communications were made:—

"On a modified form of Wheatstone's Rheostat." By Mr. SHELFORD BIDWELL.

"On a Theorem relating to Curved Diffraction-Gratings." By Mr. WALTER BAILY.

"On some Thermodynamical Relations."—Part IV. By Prof. W. RAMSAY and Dr. S. YOUNG.

May 22nd, 1886.

Prof. BALFOUR STEWART, President, in the Chair.

The following were elected Members of the Society:—

Mr. CHICHESTER A. BELL, M.B.; Mr. W. CLAUDE JOHNSON, F.R.A.S.; Mr. JAMES SWINBURNE.

The following communications were made:—

"On the Sympathetic Vibrations of Jets." By Mr. CHICHESTER A. BELL.

"On some Thermodynamical Relations."—Part V. By Prof. W. RAMSAY and Dr. S. YOUNG.

Exhibition of the Effects of Explosives by Dr. H. **Sprengel.**

Explanation by Mr. C. V. **Boys** of Thatcher's Slide-Rule, exhibited by Mr. **Stanley.**

June 12th, 1886.

Dr. J. H. **Gladstone**, Vice-President, in the Chair.

The following were elected Members of the Society:—

Mr. S. **Rideal**, B.Sc.; Mr. E. C. **Rimington.**

The following communications were made:—

"On an Electric-light Fire-damp Indicator." By **Walter Emmott** and **Wm. Ackroyd.**

"Sur la distinction entre les raies d'origine solaire et d'origine terrestre." Par Dr. le Prof. **Cornu.**

"On a Hyperbolagraph." By Mr. H. H. **Cunynghame.**

"On a Voltaic Cell with Solid Electrolytes." By Mr. **Shelford Bidwell.**

June 26th, 1886.

Prof. W. E. **Ayrton**, Vice-President, in the Chair.

The following was elected a Member of the Society:—

Mr. E. M. **Langley.**

The following communications were made:—

"On certain Sources of Error in connexion with Experiments on Torsional Vibrations." By Mr. **Herbert Tomlinson.**

"On a Mode of maintaining Tuning-Forks by Electricity." By Prof. S. P. **Thompson.**

"Further Notes on the Formulæ of the Electromagnet and of the Dynamo." By Prof. S. P. **Thompson.**

November 13th, 1886.

Prof. **Balfour Stewart**, President, in the Chair.

The death of Dr. **Guthrie**, which occurred on the 21st October, was announced.

The following communications were made:—

"On the peculiar Sunrise-Shadows of Adam's Peak in Ceylon." By the Hon. R. ABERCROMBY.

"Note on the Internal Capacity of a Thermometer." By Mr. A. W. CLAYDEN.

November 27th, 1886.

Prof. W. G. ADAMS, Vice-President, in the Chair.

The following communications were made:—

"Note on the Measurement of the Coefficient of Mutual Induction of Two Coils." By Prof. G. C. FOSTER.

"On the Stability of Liquid Surfaces of Revolution." By Prof. A. W. RÜCKER.

December 11th, 1886.

Prof. H. McLEOD, Vice-President, in the Chair.

The following were elected Members of the Society:—

Mr. W. L. NATANSON; Mr. E. NATANSON; Hon. R. ABERCROMBY;
Mr. H. M. ELDER, M.A.; Mr. JULIUS WERTHEIMER, B.Sc.

The following communications were made:—

"On the Influence of Change of State from Liquid to Solid on Vapour-Pressure." By Prof. W. RAMSAY and Dr. S. YOUNG.

"On the Nature of Liquids, as shown by a study of the Thermal Properties of Stable and Dissociable Compounds." By Prof. W. RAMSAY and Dr. S. YOUNG.

"On Cauchy's Theory of Reflection and Refraction of Light." By Mr. JAMES WALKER.

"On a Voltaic Cell in which the Electrolyte is a Dry Metallic Oxide." By Mr. SHELFORD BIDWELL.

January 22nd, 1887.

Prof. H. McLEOD, Vice-President, in the Chair.

The following was elected a Member of the Society:—

Mr. FREDERICK WOMACK, B.Sc., M.B.

The following communications were made :—

"On the Temporary and Permanent Effects on Iron of Raising its Temperature to 100° C." By Mr. H. TOMLINSON.

"On some new Measuring-Instruments used in Testing Materials." By Prof. W. C. UNWIN.

Mr. BOYS exhibited Spectrum Photographs made with Rowland's Diffraction-Grating.

The Members adjourned to Prof. UNWIN's Laboratory to inspect the new Measuring-Instruments.

Annual General Meeting.

February 12th, 1887.

Prof. BALFOUR STEWART, President, in the Chair.

The following Report of the Council was read by the President :—

In presenting their Report for the past Session, the Council have for the first time to record the loss of one of those who have taken a prominent part in the work of this Society. The death of Dr. Guthrie has been felt as a personal sorrow by all those who have attended our meetings, and especially by the members of the Council, with whom his constant presence at their meetings brought him into intimate relationship. The Society owes to Dr. Guthrie not only its foundation but that ever-ready and enthusiastic support which his genial character and scientific attainments, as well as his position as Professor of Physics in this place, rendered of the highest value.

A Committee having been formed, under the presidency of Prof. Huxley, for the purpose of raising a Memorial Fund in recognition of Dr. Guthrie's scientific labours, to be devoted to placing his children as nearly as might be possible in the position which they would have occupied but for his untimely death, and to supplementing the provision for his widow, the Council of this Society, feeling that no more suitable tribute could be offered to his memory, issued an appeal to our Members urging them to give their support to this fund; and they have been gratified to learn that this appeal has met with a liberal response.

The Council have heard with regret from Dr. Atkinson, who has filled the office of Treasurer from the foundation of the Society, that he finds himself no longer able to attend to the duties of that office. The Society owes the satisfactory state of its finances to Dr. Atkinson's watchful care, and the Council desire to express their high appreciation of his services. Members will have noticed with pleasure that Professor Rücker, who has succeeded Dr. Guthrie as Professor of Physics at the Normal School of Science, South Kensington, has consented to be nominated as a candidate for the vacant office of Treasurer. Without dwelling on Professor Rücker's high scientific reputation, the Council desire to direct attention to the fact that his election to an important office in the Society would maintain the close connexion which has existed since its foundation between this Society and the Chair of Physics, from which connexion the Society has derived very great advantages.

There has been some diminution during the past Session in the number and extent of the papers contributed to the Meetings. For example, the April, July, and November parts of our 'Proceedings' in 1885 comprised altogether 33 papers, occupying 306 pages; while the corresponding parts in 1886 comprised only 25 papers, occupying 169 pages. The Council would point out to Members the desirability of bringing forward their original work in Physics before our Meetings. A contribution to our 'Proceedings' obtains immediate publication in the columns of the 'Philosophical Magazine,' and 100 copies of the paper are sent to the author, and the papers are once a quarter reprinted and sent to all Members of our Society, so that such papers obtain a wide circulation at an early date and in a convenient form. Moreover, the use of the magnificent collection of apparatus, under the control of the Professor of Physics, is freely extended to the authors of papers for the purpose of performing experiments at our meetings, so that the experimental illustration of physical papers can be carried out at our meetings with a completeness which is elsewhere impossible.

Among the papers read during the past Session the Council desire to call particular attention to a paper by Prof. Cornu on "Solar and Terrestrial Lines in the Spectrum," one by Dr. Balfour Stewart on the "Causes of Changes in Terrestrial Magnetism," and one by Prof. Rücker on the "Stability of Liquid Films."

The Library of the Society appears to be hardly as well known to Members as it deserves; it consists of a considerable number of volumes, having been much increased in the last few years by presents from Dr. Guthrie and Lady Siemens. The Library is kept in a room adjoining the lecture-room in which our meetings are held, and books may be taken out by Members on application to the Librarian, Mr. C. V. Boys.

The second volume of Dr. Joule's works has been issued to Members, so that this undertaking is now completed.

The Council hope that the publication of Volta's works may be carried forward during the ensuing year.

The following additions have been made to the Library during the past Session:—

Proceedings of the Academy of Natural Sciences, Philadelphia.
Proceedings of the Institute of Mechanical Engineers.
Proceedings of the Royal Society.
Proceedings of the Cambridge Philosophical Society.
Proceedings of the Canadian Institute.
Scientific Proceedings of the Royal Dublin Society.
Journal of the Physico-Chemical Society of St. Petersburg.
Journal de Physique.
Journal of the Society of Arts.
Journal of the Society of Telegraphic Engineers.
Electrical Review.
Annales des Physik und Chemie.
Beiblätter des Physik und Chemie.
Séances de la Société Français de Physique.
Den Norske Nordhavs-Expedition. Zoologi: Mollusca and Crustacea.
Tokio Memoirs.
Medical and Biological Catalogue, University College, London.
Clarke's Transit Tables.

Application having been made from time to time for election to Membership of this Society by persons residing abroad, who have not been able to find any proposers personally acquainted with them, it has seemed desirable to the Council that a modification of the Bye-laws should be made so as to enable such persons to be eligible if Members of some recognized Scientific Society; and the Council have accordingly decided to propose the following addition to section 11 of the Bye-laws (under which Section personal knowledge of a Candidate is required), viz.:—

> "Provided that when a Candidate living abroad is a Member of a recognized Scientific Society such Membership may (subject to the approval of the Council) be held equivalent to the personal knowledge aforesaid."

The Council are indebted to Prof. Carey Foster for the following memoir.

By the death of Professor **Frederick Guthrie** all who have been in the habit of attending the meetings of the Physical Society will feel that they have lost a personal friend. His unfailing kindliness and geniality and his constant readiness to be helpful, without ever seeming conscious that any one owed him thanks, produced towards him a feeling of warm regard on the part of all who were in any way brought into frequent personal contact with him. Towards the Members of this Society he stood in a peculiar relation. It is seldom that a scientific Society owes its existence so distinctly to the action of one man as the Physical Society of London owes its origin to the action of Frederick Guthrie. In the summer of 1873, Guthrie invited his scientific friends and all those who, from their known tastes or official position, he thought likely to take interest in the scheme, to take steps for the formation of a Society for the cultivation of the science of Physics. The circular that he sent out ran as follows:—

> "PHYSICAL SOCIETY.
>
> "I wish to try to form a Society for Physical Research: for showing new physical facts and new means for showing old ones: for making known new home and foreign physical discoveries, and for the better knowledge one of another of those given to physical work. You who care for the being of such a Society, and are willing to help in its making, are hereby asked to write to me to that purpose before the 1st of October next. Whereupon you will be asked to meet so as to talk over the means.
>
> "Frederick Guthrie,
> 24 Stanley Crescent, Notting Hill, W."

The proposal thus quaintly made met with so much support that the Society was constituted, and held its first meeting for the reading of papers on the 21st of March, 1874. None who knew Guthrie could think that any desire for personal prominence prompted him to take the lead in establishing this Society. His account of the matter was that, by virtue of his official position he was one of those upon whom the duty of promoting the progress of Physics in London chiefly lay; and in his opinion a Society such as he proposed, and such as has come into existence, was likely to be one of the most effectual means of attaining this end. So far, the only Society in London which concerned itself directly with Physics was the Royal Society; and Guthrie thought that, without in any way interfering with the field of action of the Royal Society, there was ample room for a Society which should take cognizance of smaller matters, points of technical detail, useful laboratory contrivances, experimental methods of illustrating physical principles, questions connected with methods of teaching, and other things of much import to the advance of our science, which would nevertheless be out of place before the Royal Society. Guthrie felt also that in a Society devoted specially to Physics, the actual exhibition of physical phenomena to the members might usefully be made an important part of the proceedings. The position which the Physical Society now occupies and the value of the work it has done form the best proof of the correctness of these views. Guthrie, however, did more than merely throw out a happy suggestion at a time when many others were ready to take it up and act upon it. Without the efficient and energetic aid that he gave towards the practical realization of his idea, it is safe to say that the Physical Society would not yet have attained to its actual position of usefulness and influence among the Scientific Societies of London. Through his official connexion with the Science and Art Department, he was able to obtain from the Lords of the Committee of Council on Education permission for the Society's meetings to be held in the Physical Lecture-room of the Science Schools of the Department at South Kensington, and for the resources of the Physical Laboratory to be used at his discretion for the experimental illustration of subjects brought before the Society. More than this, he gave his time and personal efforts without stint to promoting the convenience of the authors of communications brought before the Society, and to increasing in all possible ways the interest and advantage of the Meetings.

In this room and at the first Anniversary Meeting of the Society since Dr. Guthrie's death, it is impossible, when recalling the loss we have sustained, not to remember first the genial friend who is no longer with us, and next to call to mind the almost parental relation in which he stood to the Society as a whole.

Frederick Guthrie was born in Bayswater in October 1833, and was the youngest of six children. One of his brothers, Mr. Francis Guthrie, is a distinguished mathematician, and has been for many years Principal of the South-African College, Cape Town. Guthrie received the greater part of his education at University College School and University College, London, where most of his time in the latter part of his course was given to Chemistry and Mathematics. He graduated as Bachelor of Arts of the University of

London in 1852. In the following spring he went to Heidelberg to work at Chemistry under Bunsen, and afterwards removed to Marburg in order to make a special study of Organic Chemistry under Kolbe. Here he took the degree of *Philosophiæ Doctor* in 1855. On his return to England he was appointed, in 1856, Assistant to Dr. Frankland, who was Professor of Chemistry in the then recently established Owens College, Manchester. In 1859 he became Assistant to the Professor of Chemistry in the University of Edinburgh, now Sir Lyon Playfair. After holding this appointment for about two years he went to Mauritius (in 1861) as Professor of Chemistry and Physics in the Royal College, and remained there till 1867, when he returned to England on leave. One of Guthrie's colleagues in Mauritius was Mr. Walter Besant, the eminent novelist, with whom he formed a life-long friendship. In a lecture given before the Society of Arts last February, Guthrie thus alludes to the duties which he and his friend had to discharge:—"We teachers," he says, "were expected to make ourselves generally useful. Thus, while I was supposed to teach Chemistry, Physics, and the Natural Sciences, my more gifted friend taught, amongst other things, Latin, Greek, Mathematics, and English Literature." But, however miscellaneous his official duties, Guthrie found time during this period for a large amount of valuable scientific work. In was in Mauritius that he carried out his first published physical investigations, which are recorded in three papers communicated to the Royal Society in 1864 and 1865, namely two papers "On Drops" and one "On Bubbles." These are excellent examples of purely experimental investigations, well-planned and carefully carried out. No doubt it was in his work as a practical chemist that the properties of Drops and Bubbles first attracted his attention; but it is characteristic of much of his subsequent work, and a striking evidence that he possessed the true spirit of the scientific investigator, that he saw matter for careful study and experiment in the most familiar things, instead of, like most of us, letting familiarity with the outward look of things blind him to how little accurate knowledge of them we possess.

In 1869 Guthrie was appointed Lecturer on Physics in the Royal School of Mines, and retained this post (with altered title and widened duties) till his death, which occurred, almost suddenly, from cancer of the throat, in October 1886, when he had just completed his 53rd year.

He was elected a Fellow of the Royal Society of Edinburgh in

1859 and a Fellow of the Royal Society of London in 1873. He published some forty papers on Chemistry and Physics, the Chemical papers, about one third of the whole number, being chiefly published in the first eight or nine years after his *promoviring* as Doctor. Those which followed the investigation into the properties of Drops were almost wholly physical, though many of them,—as, for example, the important series of papers entitled "On Salt-Solutions and Attached Water,"—dealt with matters which had a chemical as well as a physical aspect. Many of his principal investigations were communicated in the first instance to this Society, and may be supposed to be familiar to many of the Members. Prior to the formation of this Society, however, he had made the remarkable discovery which he described as "Approach caused by Vibration," as seen, for example, in the apparent attraction exerted by a vibrating tuning-fork on a light object suspended in the air near it. These phenomena, which were discovered independently and about the same time by Sondhaus, are closely allied to those which have been studied so elaborately, both mathematically and experimentally, in the case of incompressible fluids, by Professor Bjerknes, of Christiania, and have been followed up, in the case of air, in the beautiful experiments of Mr. Stroh.

But fertile and industrious as Guthrie was as an experimentalist, it is perhaps even more as a teacher than as an investigator that his influence will be felt hereafter. The course of work which he devised for the "Certificated Science Teachers" who came under his instruction at South Kensington was an entirely new departure in the teaching of Physics. Physical laboratories for the instruction of students had already begun to appear, but in them men were taught for the most part to use ready-made instruments. Guthrie's plan was to teach his pupils not only how to use, but how to make their instruments for themselves. Considering how absolutely the value of the system of instruction in science that has been organized under the Science and Art Department depends upon the pupils being made familiar with actual facts and phenomena, and not merely with descriptions or statements about them, it may be regarded as a matter of national importance that for the last fourteen or fifteen years every Science Teacher, who has gone through the course of Physics at South Kensington, has gone back to his classes not only with a stock of thoroughly serviceable instruments, but that he has learned how to make them for himself at a merely nominal cost, and can, if he chooses, spread the art among his pupils, and thus make his teaching of a thoroughly genuine and practical kind. How earnestly convinced Guthrie himself was of the value of this plan may be seen from his lectures on "Science Teaching," delivered before the Society of Arts last spring.

It is difficult for those who knew Guthrie well not to think of him much more as a man and a friend than as a man of science, Though he was one of the most independent and self-reliant of men both in thought and in action, in everything that concerned others he carried charity in judgment and generosity, indeed, almost to a fault. This is not the place in which to speak of his private life and affairs; but it may be said that he had to encounter difficulties such as few men have to meet, and that he faced them with such calmness and courage that most even of his intimate friends knew nothing of their existence until after his death.

In Frederick Guthrie we have lost a strong, a true, and a good man.

The Treasurer made the Financial Statement given below (pp. 15 and 16).

The Society then proceeded to the election of Officers and other Members of Council for the ensuing year. The Council was constituted as follows:—

President.—Prof. Balfour Stewart, LL.D., F.R.S.

Permanent Vice-Presidents.—Dr. J. H. Gladstone, F.R.S.; Prof. G. C. Foster, F.R.S.; Prof. W. G. Adams, M.A., F.R.S.; Sir William Thomson, D.C.L., LL.D., F.R.S.; Prof. R. B. Clifton, F.R.S.

Other Vice-Presidents.—Dr. E. Atkinson; Prof. W. E. Ayrton, F.R.S.; Shelford Bidwell, M.A., LL.B., F.R.S.; Prof. H. McLeod, F.R.S.

Secretaries.—Prof. A. W. Reinold, M.A., F.R.S.; Walter Baily, M.A.

Treasurer.—Prof. A. W. Rücker, M.A., F.R.S.

Demonstrator and Librarian.—C. Vernon Boys.

Other Members of Council.—R. H. M. Bosanquet, M.A.; W. H. Coffin; Conrad W. Cooke; Prof. G. Forbes, F.R.S.E.; Prof. F. Fuller, M.A.; Prof. J. Perry, F.R.S.; W. N. Shaw, M.A.; Prof. S. P. Thompson, D.Sc.; G. M. Whipple, B.Sc.; C. R. Alder Wright, D.Sc., F.R.S.

Votes of thanks were passed to the Lords of the Committee of Council on Education; to the President and other Officers of the Society; and to the Auditors.

THE TREASURER IN ACCOUNT WITH THE PHYSICAL SOCIETY, FROM JANUARY 1st, 1886, TO DECEMBER 31st, 1886.

Dr.	£	s.	d.	£	s.	d.
Balance in Bank, January 1, 1886				116	18	6
Subscriptions for Exhibition				3	12	0
Entrance-Fees	19	0	0			
Subscription for 1880	1	0	0			
Subscriptions for 1881	2	0	0			
" 1882	2	0	0			
" 1883	4	0	0			
" 1884	7	0	0			
" 1885	19	0	0			
" 1886	104	0	0			
" 1887	7	0	0			
17 Life Compositions	170	0	0			
				335	0	0
One year's Dividend on £400 Furness 4 per cent. Debenture Stock, less Income Tax	15	19	4			
One year's Dividend on £575 Midland 4 per cent. Preference Stock, less Income Tax	22	4	8			
One year's Dividend on £200 Lancaster Corporation Stock, less Income Tax	7	14	8			
One year's Dividend on £200 Metropolitan Board of Works Stock, less Income Tax	6	15	4			
				52	4	0
Balance due to Treasurer				3	7	8
				£511	2	2

Cr.	£	s.	d.	£	s.	d.
Due to Treasurer				5	10	4
Taylor and Francis:—						
Proceedings, vol. vii. (parts 3 and 4)	59	17	6			
Postage and addressing	7	1	0			
Members' separate copies	11	16	6			
Miscellaneous printing	12	15	10			
Joule, vol. ii.	40	0	0			
				131	10	10
Reporting to July				10	10	0
Attendance at Meetings and incidental expenses				7	9	8
Petty Cash:—						
Mr. Reinold	2	4	6			
Mr. Baily	1	0	0			
Mr. Atkinson	1	2	0			
				3	6	6
Balance in Bank				352	14	10
				£511	2	2

Audited and found correct,

E. ROBERT FESTING,
GEORGE FULLER, } *Auditors.*

London, February 12th, 1887.

PROPERTY ACCOUNT OF THE PHYSICAL SOCIETY, December 31, 1886.

Assets.	£	s.	d.	Liabilities.	£	s.	d
Balance in Bank	352	14	10	Due to Treasurer	3	7	8
Subscriptions due	100	0	0	Subscriptions for 1887	7	0	0
£400 Furness 4 per cent. Debenture Stock	456	0	0	Bills outstanding, Williams and Norgate	4	16	0
£575 Midland 4 per cent. Preference Stock	650	0	0	Index to Joule	15	0	0
£200 Metropolitan Board of Works Stock	217	0	0	Taylor and Francis, Two Parts Proceedings &c.	57	4	3
£200 Lancaster Corporation Stock	224	0	0	Due on second volume of Joule	132	13	9
Sales for 1886, per Taylor and Francis	14	0	0	Balance	1793	13	2
	£2013	14	10		£2013	14	10

We have examined the above Account, and also the Securities at the Bank, and find the same to be correct.

London, February 12th, 1887.

E. ROBERT FESTING,
GEORGE FULLER,
} *Auditors.*

157